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EFFECT OF FISH POISONS ON WATER SUPPLIES

I. REMOVAL OF TOXIC MATERIALS

II. ODOR PROBLEMS

III. FIELD STUDY - DICKINSON, NORTH DAKOTA

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CINCINNATI, OHIO

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EFFECT OF FISH POISONS ON WATER SUPPLIES

I. REMOVAL OF TOXIC MATERIALS

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EFFECT OF FISH POISONS ON WATER SUPPLIES

I. Removal of Toxic Materials

INTRODUCTION

The recreational use of water supply reservoirs was accepted in a recent statement of policy by the American Water Works Association Board of Directors on January 26, 1958, that "(1)....recreation is considered permissible under appropriate sanitary regulation."

Sport fishing is one of the more popular recreational uses of reservoirs. To increase the attractiveness of this sport, practically all states have undertaken fish management practices. Fisheries managers sometimes find it expedient to remove an entire fish population from a body of water (2) to eliminate stunted populations or coarse fish and to enable restocking with fry or fingerlings of suitable species. The young fish, freed from predation and competition for food, make rapid growth and provide superior sport fishing.

Much work has been done on the development of suitable piscicides until today there are many commercial preparations on the market. Cost, ease of application, safety, and effectiveness in destroying fish populations are the major considerations in the selection of a compound .

The deliberate addition of a fish toxicant to a water supply source requires careful appraisal of its effect on water quality and safety. The practice demands consideration of the following possible effects:

1. Toxicity of active agents to humans, other mammals, and to fish in household aquaria.
2. Effects of fish poison formulation and components on water treatment processes and conversely the effects of treatment on these compounds.
3. Tastes and odors produced by the components of the formulation.
4. Effects on water quality which may result from decomposing fish.)

TOXICITY OF ROTENONE AND TOXAPHENE

The principal toxic agents in the fish poison formulations in common use are rotenone and toxaphene.

Toxicity of Rotenone to Mammals

The acute toxicity of rotenone by the oral route is unusual in that it is marked by a wide variation among species ⁽³⁾ varying from ⁽⁴⁾ approximately 60 mg/kg for the guinea pig, 130 mg/kg for the albino rat, approximately 1.5 g/kg in rabbits, to approximately 3 g/kg in dogs. ⁽⁵⁾

The effects from acute single oral doses consist of severe irritation of the gastrointestinal tract; in dogs, cats, and pigeons emesis accompanies a toxic dose. On an acute oral basis rotenone would be classed according to a conventional system as bordering on the "highly toxic" for the guinea pig but only "slightly toxic" for the rabbit and dog.

Rotenone is far more acutely toxic by other routes of administration either intraperitoneally or intravenously, 2 mg/kg being the acute LD₅₀ for the guinea pig intraperitoneally, and 0.65 mg/kg for the dog and cat intravenously when the rotenone was administered in ethylene glycol; on the basis of dose administered, ethylene glycol was considered to be noninjurious in control animals.⁽³⁾

Chronically administered during a two-year period in the diet of rats, rotenone produces necrosis in the liver at a level of only 5 parts per million;⁽⁶⁾ the same degree of tissue damage would require about 2 times the dose of mercuric acetate, a well-recognized cellular poison. On a diet of 150 milligrams rotenone/kg of food, fetuses of pregnant guinea pigs either failed to survive until birth, or died shortly thereafter.⁽³⁾

Because no reports exist of man being poisoned by rotenone, it is assumed that man is one of the more highly resistant species. The

fact that man has eaten fish killed by rotenone unfortunately provides no evidence on this point because the peculiar injury of rotenone to the gills of fish makes it doubtful that any significant amount would enter the fleshy part of the fish that is eaten. The fact that rotenone has been used as a spray on edible foods likewise provide no evidence of its lack of toxicity for man because its instability in air and sunlight causes the destruction of a major portion of the residue on such foods before they are eaten.

Toxicity of Toxaphene to Mammals

Toxaphene is one of the more toxic of the chlorinated hydrocarbon insecticides to mammals. The acute oral LD₅₀ for rats is about 40 mg/kg and for dogs, 10 to 15 mg/kg. In chronic feeding tests, dogs fed toxaphene at a level of 60 ppm in the diet for 106 days showed degenerative changes in the liver and other organs.⁽⁷⁾

In addition to toxaphene and rotenone the common formulations contain solvents of unknown chemical composition and toxicity.

Although there is little likelihood that these formulations would cause toxic manifestations in humans when used in the concentration needed to kill fish, they are distinctly undesirable in drinking water and should be removed or chemically altered in order to produce a finished water of good quality.

Since little information is available in the literature on the ability of water treatment processes to remove or alter these materials, laboratory investigations were undertaken. Accordingly, the following investigations were made on fish poison formulations and their components:

1. Removal by activated carbon.
2. Chemical detoxification by chlorine and chlorine dioxide.
3. Removal by alum coagulation.
4. Production and removal of odors.

FISH POISONS

Traditionally, the preferred fish poison has been derris⁽⁸⁾ or cube⁽⁹⁾⁽¹⁰⁾ ground root, or rotenone which may be extracted from these plant materials. Difficulty in handling and evenly applying powdered root and the high cost of rotenone have led to the development of various commercial formulations which incorporate rotenone, rotenoid extractives, various hydrocarbon solvents, wetting agents, and inert materials such as clay. Other fish poisons such as toxaphene, and synergists such as sulfoxide (n-octyl sulfoxide of isosafrole) have also been employed.

The following fish poisons and formulations were selected for this study:

- (a)
1. Rotenone
- (b)
2. Toxaphene
- (c)
3. Powdered Cube Root

-
- (a) Obtained from Chemical Insecticide Corp., C. P. Grade.
 - (b) Obtained from Hercules Powder Co. Reference standard containing 68% chlorine.
 - (c) Obtained from S. B. Penick Company

(c)

4. Sulfoxide Tech., containing a minimum of 88% (n-octyl sulfoxide of isosafrole) and a maximum of 12% related compounds.
5. Formulation A, containing the active ingredients 2.0% rotenone and 7.0% toxaphene.
6. Formulation B, containing the active ingredients 5% rotenone and 15% other cube¹ extractives.
7. Formulation C, containing the active ingredients 2.5% rotenone, 5% cube¹ extractives, and 2.5% sulfoxide.
8. Formulation D, containing the active ingredients 5% rotenone and 10% other cube¹ extractives.

These formulations contain, in addition to the active poison, inert materials such as solvent, emulsifying agent, or mineral carrier.

All of the formulations were studied at 2.0 mg/l concentration. Lesser concentrations, depending on the aqueous solubility, were used for the components.

RESIDUE ANALYSES

Initial attempts to use chemical methods for quantitative determination of rotenone and toxaphene in water proved unsuccessful with the low concentrations involved. A bioassay, based on the extreme sensitivity of fish to these compounds, was used to determine the amount of compound remaining after various treatments.

The validity of bioassays using various test animals is well documented and excellent reviews have been published by Yun-Pei-Sun⁽¹¹⁾⁽¹²⁾ and Dewey. The technique in this laboratory consisted of establishing a standard curve relating concentration of chemical to time of loss of equilibrium of 50% of the test fish. By introducing fish into unknown concentrations under the test conditions, quantitative determinations of the concentrations could be obtained by reference to the standard curve.⁽¹³⁾

In this study standard curves were prepared using a logarithmic series of concentrations, e.g. 0.1, 0.18, 0.32, 0.56, 1.00, etc., mg/l of fish poison in the test water. Five fathead minnows (Pimephales promelas) of fairly uniform size, 2 to 2½ inches long and weighing 1 to 1½ grams each were added to duplicate 10-liter quantities of each concentration in 5-gallon, wide-mouth, glass bottles. Temperature was maintained at 25° C. Observations were made of the time necessary for 50% of the fish to lose equilibrium. Time was then plotted against concentration on log-log paper. Typical standard curves obtained on pure compounds

are shown in Figure 1. It is immediately apparent that fish are highly sensitive to rotenone, and far less so to sulfoxide. Analyses for residues of rotenone can easily be made down to 0.006 mg/l.

The degree of treatment needed for the removal of fish poisons in a raw water supply was based on the assumption that the finished water would contain no detectable toxicity to the test fish. In this study, removal of toxicity was considered to be complete when residual concentration of toxicants was numerically one-half of the 96-hour TL_m (median tolerance limit) value for these compounds. The TL_m value was (14) determined according to Doudoroff et al, and is defined as the concentration of toxicant at which 50% of the test fish are able to survive. One-half of the 96-hour TL_m concentration is an arbitrary value selected for computation purposes. These concentrations are presumed to be nontoxic to fish. The values for all of the fish poisons and components tested are listed in Table I, along with the concentration representing one-half of the 96-hour TL_m value.

EXPERIMENTAL

SOLUBILITY

Both rotenone and toxaphene, the principal toxicants in commercial formulations, have been reported as practically insoluble in water. (15)
Solubility of rotenone has been reported by Jones and Smith to be 0.16 mg/l. No data were available for the solubility value of toxaphene.

Table I
Acute Toxicity Values for Fish Poisons
to Fathead Minnows

Toxicant	96-hour TL_m in mg/l	One-half of 96-hour TL_m in mg/l
Toxaphene	0.013	0.007
Rotenone	0.006	0.003
Cube Root	0.066	0.03
Sulfoxide	0.74	0.37
Formulation A	0.10	0.05
Formulation B	0.066	0.03
Formulation C	0.066	0.03
Formulation D	0.10	0.05

In order not to exceed the solubility of these materials in the experimental work, values for both in distilled water at 25° C were determined by suspending a large excess of each toxicant in distilled water and stirring for several hours at the constant temperature of 25° C. Undissolved material was removed by filtration through a molecular filter with an 0.8 micron pore size. Concentration of each toxicant in the filtrate was obtained by fish bioassay. Solubility values obtained in this manner were 0.4 and 0.17 mg/l for toxaphene and rotenone respectively. Because of their extreme toxicity to fish, the very low water solubility of these materials is not a deterrent to their use as a fish poison.

In the experimental work the initial concentration of toxicant never exceeded these solubility values. Use of 2.0 mg/l of commercial formulation in all cases yielded concentrations of rotenone or toxaphene well below the aqueous solubility of these compounds.

ACTIVATED CARBON TREATMENT

Treatment with activated carbon offers the water plant one of the most effective processes for removing small amounts of organic material. Hence, this process of removing fish poisons from raw water was studied in detail.

Test water in all of the experimental work was a clear, hard, highly mineralized spring water, diluted 1 to 4 with distilled water. Chemical characteristics were pH 8.3, alkalinity 80 mg/l, hardness 90 mg/l, and turbidity 0.5 units. The activated carbon was Aqua Nuchar A*, a grade widely used in water treatment. All tests were made at ambient temperatures of 23 to 26° C.

The laboratory procedure consisted of adding varying amounts of carbon to fixed concentrations of contaminant. The suspensions were stirred rapidly for 30 minutes at 25° C. Carbon was removed from suspension by filtration through a glass column packed with fine glass

* Obtained from West Virginia Pulp and Paper Co., Tyrone Pa.

wool. (Tests had shown that glass wool does not remove detectable amounts of fish poison.) The filtrate was analyzed by fish bioassay for residual poison. Data were then used to plot an adsorption isotherm according to Freundlich's equation, usually written as:

$$1. \frac{X}{M} = KC^{1/n}$$

in which X equals units of adsorbate held by the carbon and M equals the carbon weight by which adsorption was effected. C equals concentration of substance remaining unadsorbed at equilibrium. The two parameters K and $1/n$ are particular to the system, i.e. to both the carbon used and the nature of the adsorbate. The equation thus correlates adsorbate removed per unit weight of carbon, $\frac{X}{M}$, with concentration of adsorbate remaining in solution at equilibrium, C. The equation in logarithmic form appears as:

$$2. \log \frac{X}{M} = \log K + 1/n \log C$$

which is an equation of a straight-line having a slope of $1/n$ and an intercept of K at $C = 1$.

Typical raw data to construct a carbon adsorption isotherm are shown in Table II where a toxaphene solution, 0.3 mg/l, was treated with different amounts of carbon. These data, when plotted on log-log paper, produce a straight line. Calculation of the parameters K and $1/n$ for this line then provides the means to predict the dose of carbon required to reduce any concentration of toxaphene to any desired level.

TABLE II

Adsorption of 0.30 mg/l Toxaphene
by Activated Carbon

M	C	X	$\frac{X}{M}$
mg/l Carbon	mg/l Toxaphene Residual	mg/l Toxaphene Adsorbed	mg/l Toxaphene Adsorbed per mg/l Carbon
0	0.30	-	-
1.0	0.18	0.12	0.12
2.0	0.16	0.14	0.07
3.0	0.085	0.215	0.072
6.0	0.058	0.242	0.040
9.0	0.014	0.286	0.032

Value of parameters: $K = 0.16$

$1/n = 0.42$

Carbon adsorption isotherms were obtained for the commonly used toxicants (Figure 2), and for the commercial fish poison formulations, (Figure 3).

Usefulness of the Freundlich equation and the isotherm lies in the computation and graphs which may be derived from them. Thus, for day-to-day plant use, it may be desirable to know the amount of carbon required to reduce any quantity of fish poison to a predetermined level. This is done by taking advantage of a characteristic of the Freundlich equation. If for X we use its equivalent $C_0 - C_f$, where C_0 equals initial concentration of poison and C_f equals the permissible residual poison, the equation then becomes:

$$3. \quad \frac{C_o - C_f}{M} = KC_f^{1/n}$$

This equation is linear when M is plotted against C_o on ordinary coordinate paper.

These computations were made for all of the pure components and for the fish poison formulations using the parameters derived graphically from the adsorption isotherms shown in Figures 2 and 3. The value for C_f , or permissible residual concentration of fish poison at equilibrium following carbon treatment, was taken as one-half of the 96-hour TL_m values (Table I.). The plots in Figure 4 give the amounts of carbon required to reduce any concentration of fish poison to the selected permissible residual concentration.

Amounts of carbon required for toxaphene and rotenone are similar. Among the commercial fish poisons, Formulation A is the most easily removed, 8.8 mg/l of carbon being required to reduce 2.0 mg/l of the formulation to 0.05 mg/l. The natural product, cube root, is also easily removed. At the other extreme, it would require 26.4 mg/l of carbon to reduce Formulation B to a residual of 0.03 mg/l.

CHLORINE TREATMENT

Many investigators have observed that rotenone is easily oxidized
(8)
when exposed to air and light. It is also readily oxidized by chemical
(16)
agents such as potassium permanganate. Lawrence demonstrated that

2.0 mg/l of potassium permanganate can detoxify 1.0 mg/l of NoxFish (equivalent to 0.05 mg/l of rotenone). Oxidation with permanganate is rapid. Fish survived in water to which rotenone and potassium permanganate were added at the same time. Since chlorination is common in practically all water treatment plants, this process was studied for its effect on the fish poisons which include the pure compounds and the commercial formulations.

Varying amounts of chlorine were added to test water (same procedure as for carbon experiments) containing known amounts of fish poisons and the solutions were allowed to stand at a constant temperature of 25° C. At the end of varying times of contact, sufficient sodium thiosulfate was added for dechlorination purposes, and the water was then subjected to fish assay to determine residual fish poison.

Typical laboratory data are shown for rotenone in Table III. In these tests 0.1 mg/l of rotenone was treated with varying amounts of chlorine solution for three different periods of contact at 25° C. The solutions varied in pH from 7.2 to 8.3. It is clear from these data that the effectiveness of chlorine as a detoxification agent is dependent both on the dose and time of contact. To reduce an initial concentration of rotenone of 0.1 mg/l to 0.005 mg/l or less requires 38.5, 29.5, and 11.0 mg/l of chlorine at contact times of 15, 60, and 180 minutes respectively.

TABLE III

Chlorine Treatment of 0.1 mg/l
Rotenone Solution

Contact Time - Minutes					
15		60		180	
Chlorine Applied mg/l	Rotenone Residual mg/l	Chlorine Applied mg/l	Rotenone Residual mg/l	Chlorine Applied mg/l	Rotenone Residual mg/l
4.3	0.09	1.5	0.07	0.73	0.085
10.5	0.064	7.4	0.06	1.5	0.07
17.5	0.058	14.8	0.02	2.2	0.06
21.0	0.042	22.1	0.01	4.4	0.04
24.5	0.023	29.5	< 0.005	7.3	0.013
31.6	0.012	44.3	< 0.005	11.0	0.005
38.5	< 0.005			18.3	< 0.005
56.1	< 0.005			21.9	< 0.005

These data may also be plotted, as shown in Figure 5, to provide by extrapolation an estimation of the amount of chlorine required to reduce the toxicity of 0.1 mg/l of rotenone to one-half of the 96-hour TL_m . These data show that 41.5, 30.0 and 11.5 mg/l of chlorine would be required for contact times of 15, 60, and 180 minutes respectively to detoxify 0.1 mg/l of rotenone solution to the above level.

Treatment of 0.3 mg/l of toxaphene with up to 200 mg/l of chlorine for 180 minutes showed no reduction in toxicity to fish. Toxaphene, as would be expected of a highly chlorinated hydrocarbon, is completely inert to additional treatment with aqueous chlorine solution.

No attempt was made to treat sulfoxide with chlorine since the 96-hour TL_m value for fish, 0.74, is well above the concentration likely to be present in a water treated with any fish poison formulation. For example, treatment of a water with 2 mg/l of Formulation C would yield a concentration of 0.05 mg/l of sulfoxide.

Commercial fish poison Formulations A, B, C, and D in a concentration of 2 mg/l were also treated with increasing amounts of chlorine for various contact times. The data were then plotted according to Figure 5 and the curves extrapolated to obtain the amounts of chlorine required to reduce the toxicity to one-half of their 96-hour TL_m value. The close agreement of the values for Formulations B, C, and D, (Table IV) indicates the presence of a common toxic agent. These formulations, previously described, depend primarily for their toxicity to fish on rotenone and other extractives obtained from the natural products, cube and derris roots. The values for chlorine requirements for 2.0 mg/l of the formulations are roughly comparable to that for 0.1 mg/l of pure rotenone, since the formulations contain approximately 5% rotenone. The observed differences may be explained by variations which may be expected in a commercial formulation and by the fact that, in addition to rotenone, some formulations contain other root extractives and synergists. Derris and cube¹ extractions yield materials less active physiologically to fish than pure rotenone.

TABLE IV

Amounts of Chlorine Required to
Reduce 2.0 mg/l of Fish Poison
Formulations to One-Half of 96-Hour TL_m

Mg/l of Chlorine Required					Rotenone 0.1 mg/l
Contact Time Minutes	Formulation B	Formulation C	Formulation D		
15	32	34	38		41.5
60	21	20	21		30
180	15	12	10		11.5

Chlorination of Formulation A revealed the presence of both rotenone, which is oxidized by chlorine, and toxaphene, which resists any action by chlorine. Thus, the curves for the chlorination of 1.0 mg/l of Formulation A, (Figure 6), demonstrate that toxicity due to the rotenone content can be reduced with about 2 to 4 mg/l of chlorine with a contact time of 180 minutes, although this solution remains toxic to fish because of the unaffected toxaphene content.

Application of substantial amounts of chlorine offers a means for removing the toxicity of some commercial fish poison formulations particularly those containing only rotenone or rotenoid compounds as the active ingredient. Formulations which include other toxic agents, such as Formulation A which contains 7% toxaphene, are resistant to any amount of

chlorine application and may be removed from solution only by activated carbon. Since a large excess of chlorine is required to detoxify rotenone, some means must be provided for dechlorination before the water may be distributed to the consumer.

CHLORINE DIOXIDE TREATMENT

Chlorine dioxide is a powerful oxidizing agent and has been found effective in controlling some taste and odor problems. On a weight basis, expressed in terms of available chlorine, it has, theoretically, $2\frac{1}{2}$ times as much oxidizing capacity as chlorine. Since rotenoid compounds are particularly sensitive to oxidation, use of chlorine dioxide for this purpose appeared to offer a promising method of treatment.

A 0.1 mg/l solution of rotenone was prepared in chlorine dioxide demand-free water and then treated with varying amounts of chlorine dioxide. The reaction was allowed to proceed for 15, 60, and 180 minutes at 25° C. Following dechlorination with sodium thiosulfate, residual rotenone was determined by bioassay. It is clearly evident from the data, (Figure 7), that chlorine dioxide is an effective oxidant for rotenone. Figure 7 indicates that the amounts of chlorine dioxide which must be applied to a 0.1 mg/l solution of rotenone to reduce the toxicity to one-half of the 96-hour TL_m for fish (0.003 mg/l of rotenone) range from 0.88 mg/l for a contact time of 15 minutes to 0.50 mg/l for 180 minutes.

Doses of chlorine dioxide up to 7.9 mg/l had no effect on 0.3 mg/l of toxaphene even after a contact time of 180 minutes.

ALUM COAGULATION

Alum coagulation failed to remove either rotenone, toxaphene, or the commercial formulations. Treatment of these compounds with up to 100 mg/l of alum produced no significant reduction in concentration.

STABILITY

Knowledge of the stability of the fish poisons is important, since the degree of stability will determine the required duration of special water treatment. It is obvious that detoxification of the fish poison by natural agencies in a water will impose a shorter period of concern in a water plant.

Rotenone is readily detoxified by the action of light and air, and the rate of decomposition is proportional to the log of the light energy.⁽¹⁷⁾
⁽¹⁸⁾ Subba-Rao and Pollard reported that almost all rotenone toxicity is lost in five to six spring days, or two to three summer days. In a laboratory experiment Leonard⁽⁸⁾ found that the toxicity of rotenone, added as 1.0 mg/l derris suspension, had dissipated at 60° F in 20 to 41 hours. He further found that a 1% powdered derris root suspension in water lost between 60% and 75% of its toxicity in 34 days.

⁽⁹⁾ Field observations by Smith showed that 1.33 mg/l of derris remained toxic to fish for one month but was nontoxic in 35 days. Twenty-eight days after treating a large lake with 1.8 mg/l of a commercial⁽¹⁹⁾ formulation, Hoffman and Payette were able to restock with fish.

Alkalinity seems to be important to the persistence of rotenone, since
(10)
Clemens and Martin showed that the toxicity of a concentration of 0.5
to 0.3 mg/l of a 5% rotenone emulsion was lost in 1 to 3 days in water
which had a methyl orange alkalinity of 60 to 284 mg/l, while 3 to 6
days were required in waters of low alkalinity such as 16 mg/l.

Low temperatures and exclusion of air and light, under ice cover,
markedly decrease the rate of decomposition so that a lake, treated with
a rotenone preparation, under the above conditions, remained lethal to
(20)
fish for 5 months.

Thus rotenone is a fairly labile compound whose maximum life
in a natural water may be more than 5 months under conditions adverse
for decomposition but is generally much less than a month under more
favorable conditions.

The introduction of toxaphene as a practical fish poison is
relatively recent and hence much less is known about its persistence in
natural waters. The reported length of time a water remains toxic after
treatment with toxaphene varies, ranging from a minimum of 4 weeks, as
(21) (20)
reported by Hemphill to a maximum of more than 2½ years. Within these
(22)
extremes, Tanner and Hayes showed that two lakes treated with 0.1 mg/l
toxaphene remained toxic for 7 and 10 months. Detoxification of
(23)
toxaphene was reported by Hooper and Grzenda to depend on exposure to
light, dissolved oxygen content, and temperature. Hard water detoxified

more rapidly than soft and toxicity reduction was greatly accelerated by water movements which brought the toxicant into contact with the walls and bottom of the aquarium. Rate of detoxification was increased by the presence of solid surfaces such as sand and mud. The authors also concluded that microorganisms are capable of detoxifying toxaphene. Under field conditions, toxaphene was found to retain toxicity for long periods. Ten Michigan lakes, after treatment with a fish poison formulation containing toxaphene, remained toxic for 8 to 33 months and in another field trial, from 2 to 10 months.

Extreme stability of toxaphene in a sandy soil was demonstrated by (24) Hetrick who found that toxaphene retained its toxicity to termites after 10 years in sandy soil.

From the limited experience on the stability of toxaphene in water, it seems clear that toxicity will persist for much longer periods than rotenone, perhaps for as long as 33 months.

PRODUCTION OF ODORS

In addition to the problem of removing toxicity, the water treatment plant may have to contend with removal of odors associated with the use of a fish poison formulation containing hydrocarbon solvents. Toxaphene is a very odorous compound and would certainly have to be removed for this reason alone, if not for reasons of toxicity.

A detailed study was made on the odor aspects of fish poison formulations in water and will be reported in a subsequent paper. In the following discussion, only the removal of toxicants is considered.

SUMMARY AND DISCUSSION

Fish management in a water supply reservoir by application of chemical agents toxic to fish appears to be consistent with the objective of a water treatment plant: namely, to produce a safe and potable water. The inescapable criteria of safe and potable finished water following treatment may be achieved by (1) proper selection of a fish poison, and (2) use of the most effective treatment process, coupled with close quality control.

Although both rotenone and toxaphene are relatively toxic and their routine use in water supplies would be regarded with disfavor, their occasional use for fish management should present no hazard if adequate measures are taken for their removal by treatment or by decomposition through natural processes.

The doses of chemicals required to produce satisfactory finished water in the laboratory investigations are summarized in Table V. In all of these data, good water quality was presumed to be attained when the concentration of toxic components of fish poison had been reduced or altered to a value of one-half of its 96-hour TL_m as shown in Table I.

The chemical doses shown represent the amounts determined under laboratory conditions and are useful only for comparative purposes. The amount of treatment chemical required under practical conditions, which are special to any water plant and water quality, cannot be predicted from these laboratory data. However, these data can be considered useful for predicting the treatment most likely to produce a safe finished water.

SELECTION OF FISH POISON

On the basis of ease of removal of the compounds studied the logical choice of the most suitable fish poison would be pure rotenone. This chemical is easily removed by moderate amounts of activated carbon and by reasonable amounts of chlorine when three hours of contact time are available. The necessity to dechlorinate, however, mitigates against this latter method of treatment. Treatment with chlorine dioxide offers another means for rotenone detoxification. The rapid disappearance of rotenone in the reservoir from natural causes ensures a relatively short critical period at the water treatment plant.

Cube¹ powder and any of the formulations which contain only rotenone or rotenoid materials would be a desirable fish poison. The amounts of treatment chemicals required for these are somewhat higher than those required for pure rotenone because the formulations contain in addition to rotenone, rotenoid extractives, synergists such as sulfoxide and emulsifiers, all of which add to the burden of removal.

TABLE V

Summary of Data on Treatment of
Water Containing Fish Poisons

Fish Poison	Initial Concentration mg/l	Carbon (a) Treatment	Chlorine (a)			Chlorine (a) Dioxide Treatment	Alum Coag.	Estimated Comparative Stability (d)
			15	60	180			
Rotenone	0.1	6.6	41.5	30	11.5	0.88-0.50	ng ^(c)	1 month
Toxaphene	0.1	5.0	ng	ng	ng ^(c)	ng ^(c)	ng	1 year
Cube Powder	2.0 ^(b)	9.8	-	-	-	-	ng	1 month
Formulation A	2.0	8.8	ng	ng	ng ^(c)	-	ng	1 year
Formulation B	2.0	26.4	32	21	15	-	ng	1 month
Formulation C	2.0	21.6	34	20	12	-	ng	1 month
Formulation D	2.0	16.7	38	21	10	-	ng	1 month

(a) Concentration of reagent in mg/l required to reduce fish poisons to one-half of 96-hour TL_m value.

(b) 2.0 mg/l of cube powder containing 5% rotenone is equivalent to 0.1 mg/l of rotenone, although other toxic rotenoid compounds are also present.

(c) Not effective in removing fish poison.

(d) See discussion on stability for reported data.

Use of toxaphene or formulations containing toxaphene would present to the water treatment plant the burden of removing practically all of the toxaphene since no natural dissipation in the reservoir can be expected in a reasonable time. Treatment with activated carbon would have to be continuous at a sustained high level, in view of toxaphene persistence, until the entire contents of the reservoir had gone through the water plant, or until dilution with uncontaminated water had reduced the concentration. No common treatment other than activated carbon will remove toxaphene; both chlorine and alum coagulation are completely ineffective.

SELECTION OF TREATMENT PROCESS

The single most effective water treatment process for removing fish poisons from a water supply is unquestionable activated carbon. Activated carbon will remove not only rotenone and toxaphene types, but also the solvents and emulsifiers present in all of the commercial formulations. This broad spectrum activity also eliminates odors, which will be discussed in a subsequent paper.

Chlorine and chlorine dioxide are effective against rotenone and rotenoid compounds, but some means must be provided for removing the substantial residual chlorine. Chlorination, however, has practically no effect on the other materials in fish poison formulations and, hence, recourse to activated carbon must be made to eliminate the odors due to these materials.

Alum coagulation has proved to be completely ineffective in removing fish poisons from water.

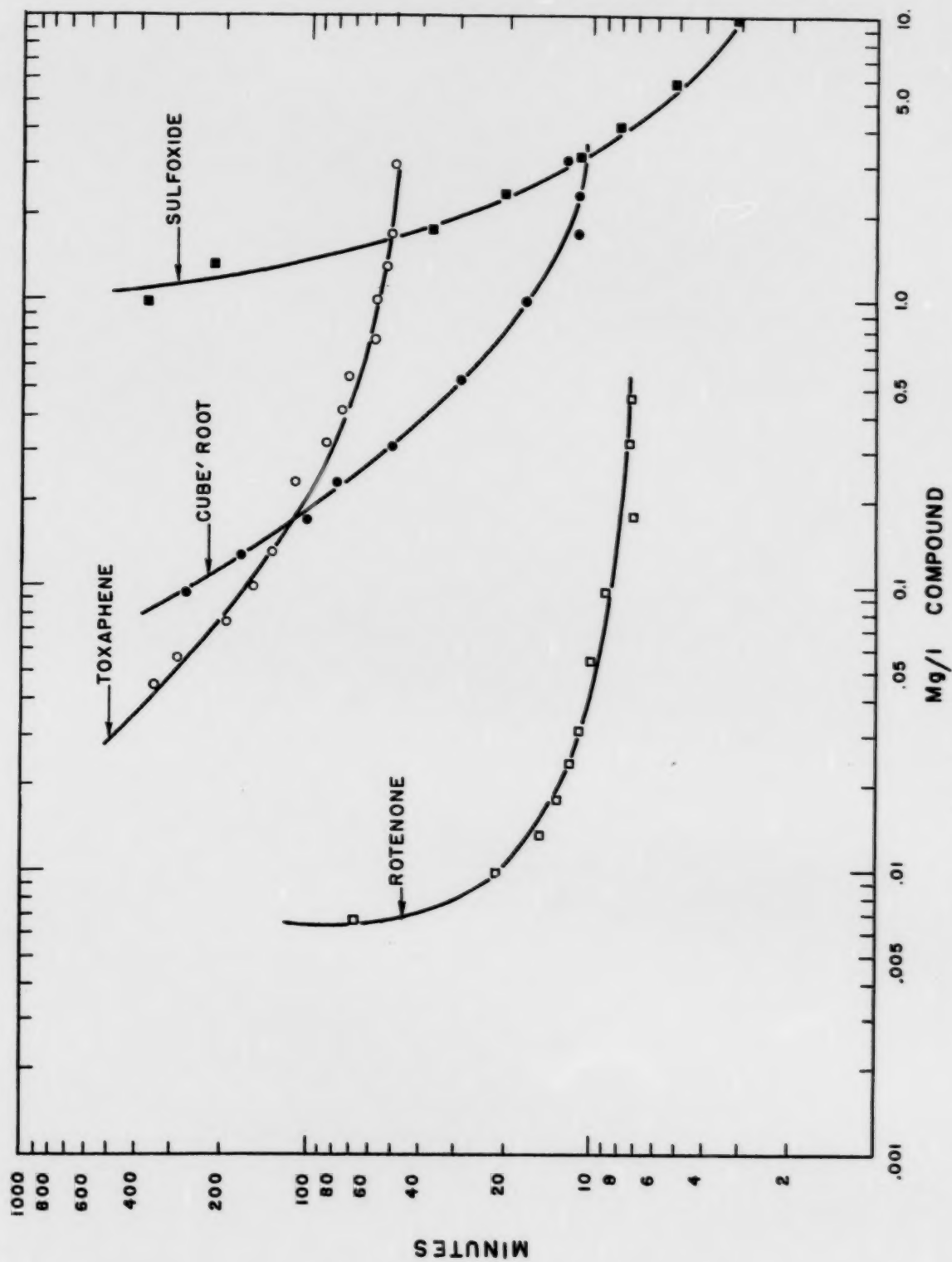
ACKNOWLEDGMENTS

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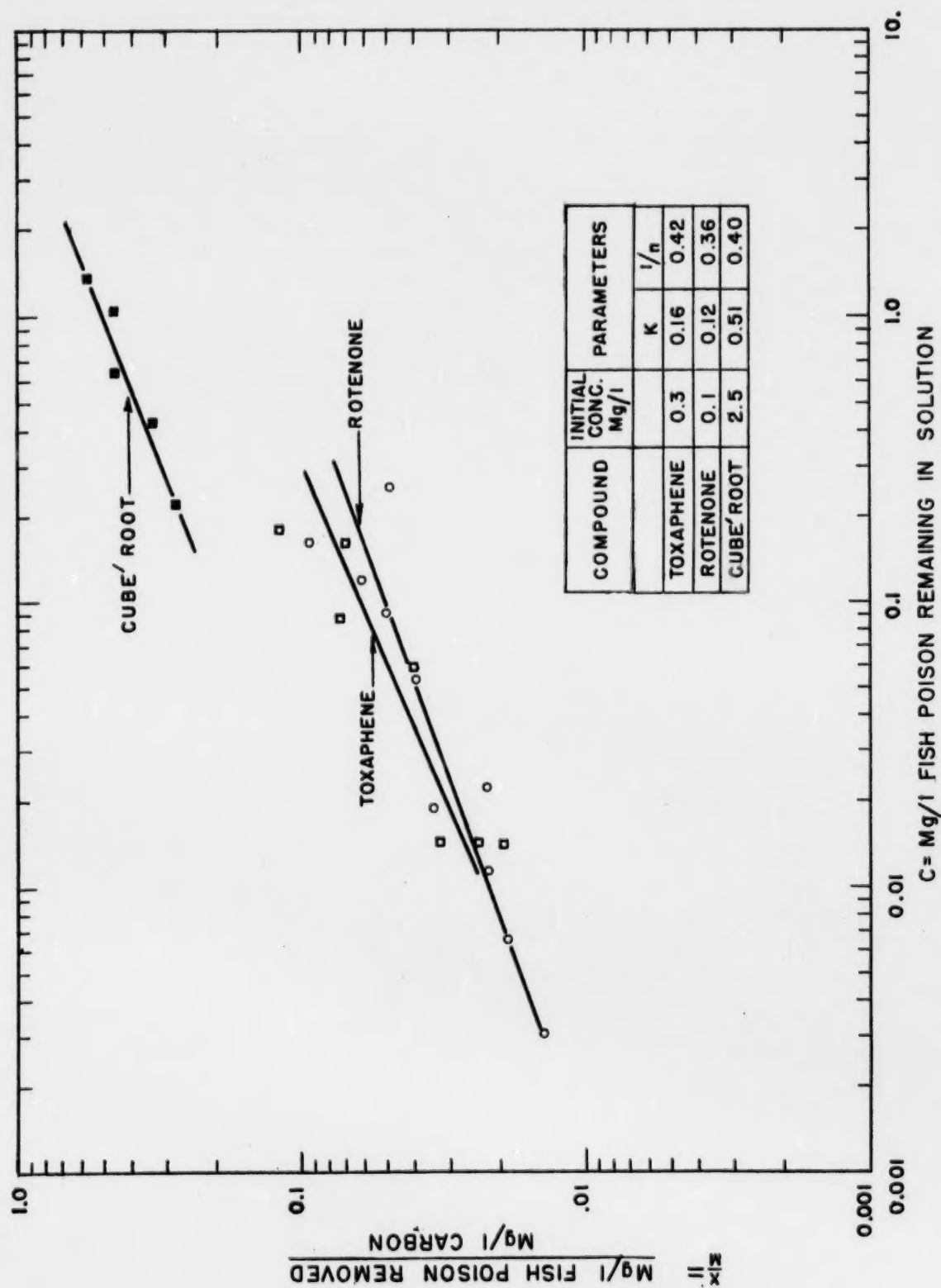
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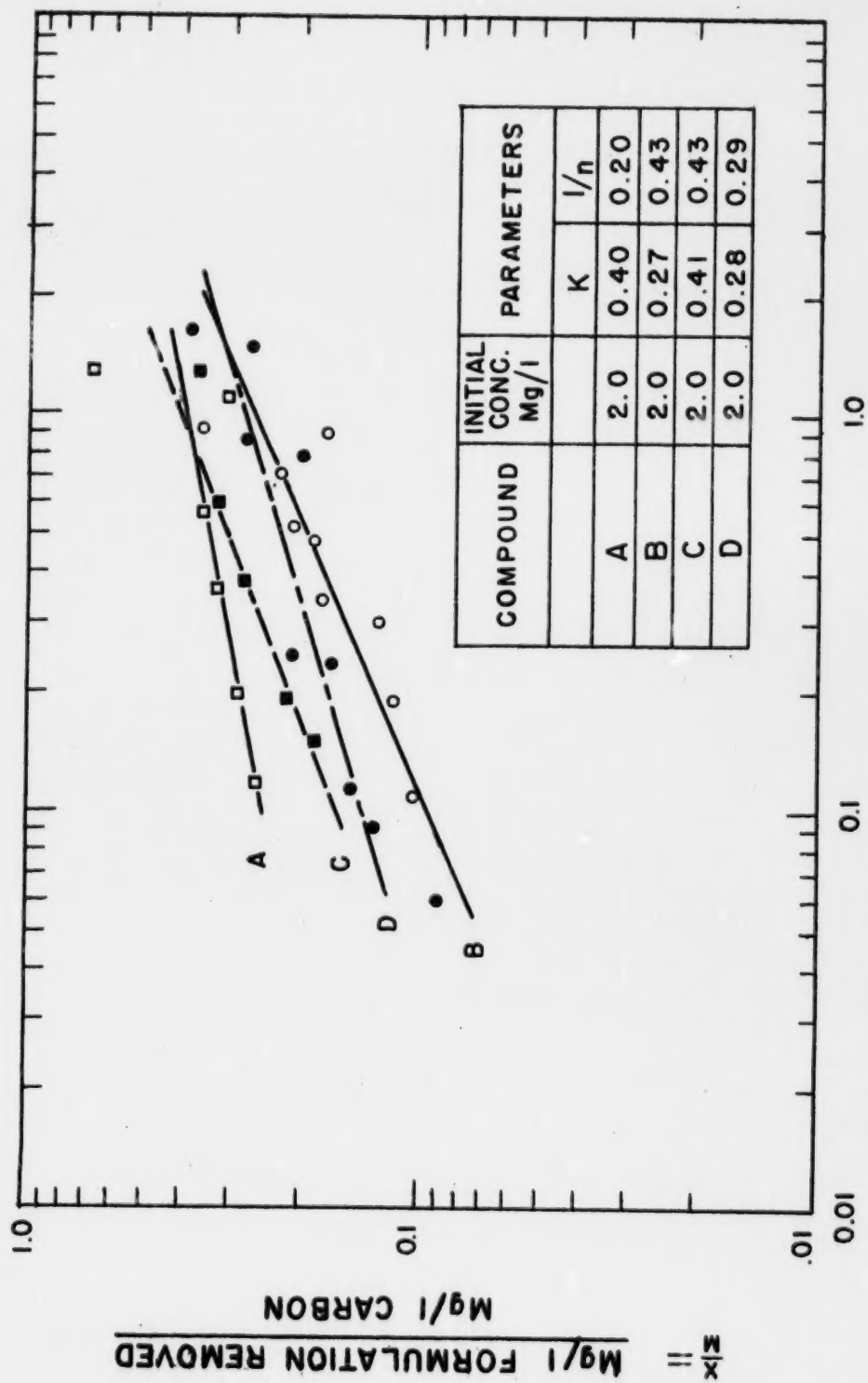
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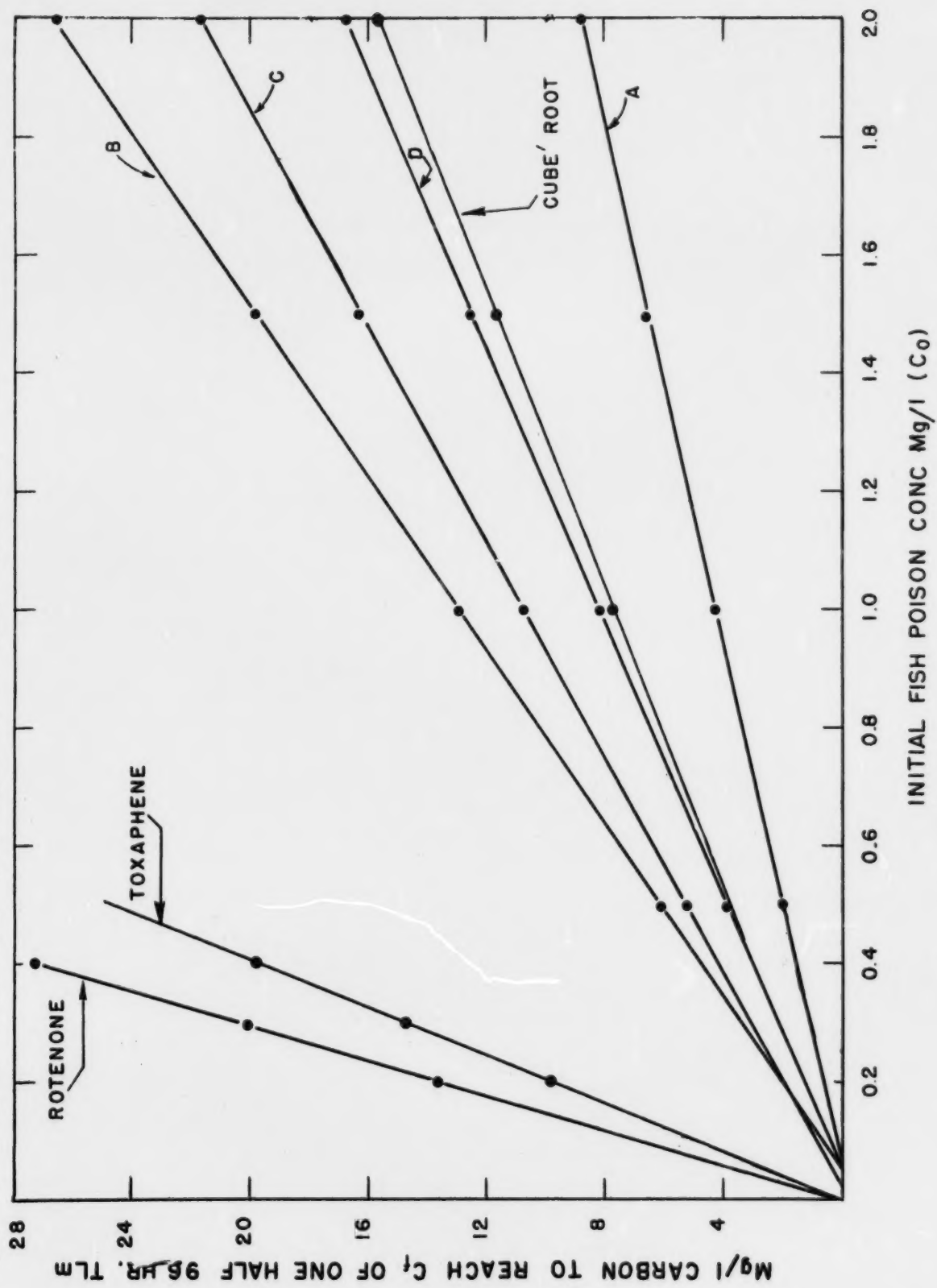
CONCENTRATION-RESPONSE CURVES FOR PURE COMPOUNDS



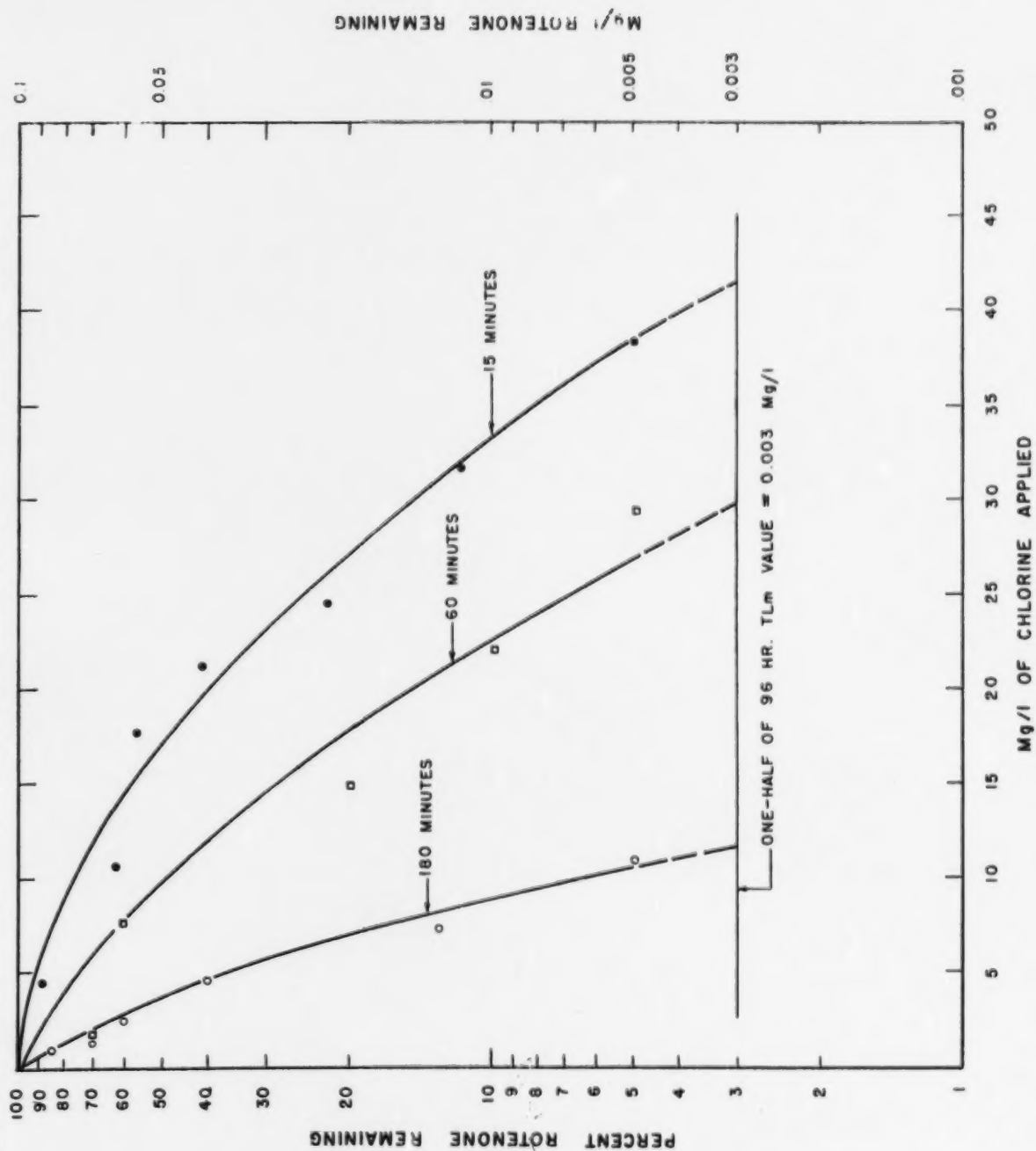
CARBON ADSORPTION ISOTHERMS FOR PURE FISH POISONS



C = Mg/l FISH POISON FORMULATION REMAINING IN SOLUTION
 CARBON ADSORPTION ISOTHERMS FOR COMMERCIAL
 FISH POISON FORMULATIONS

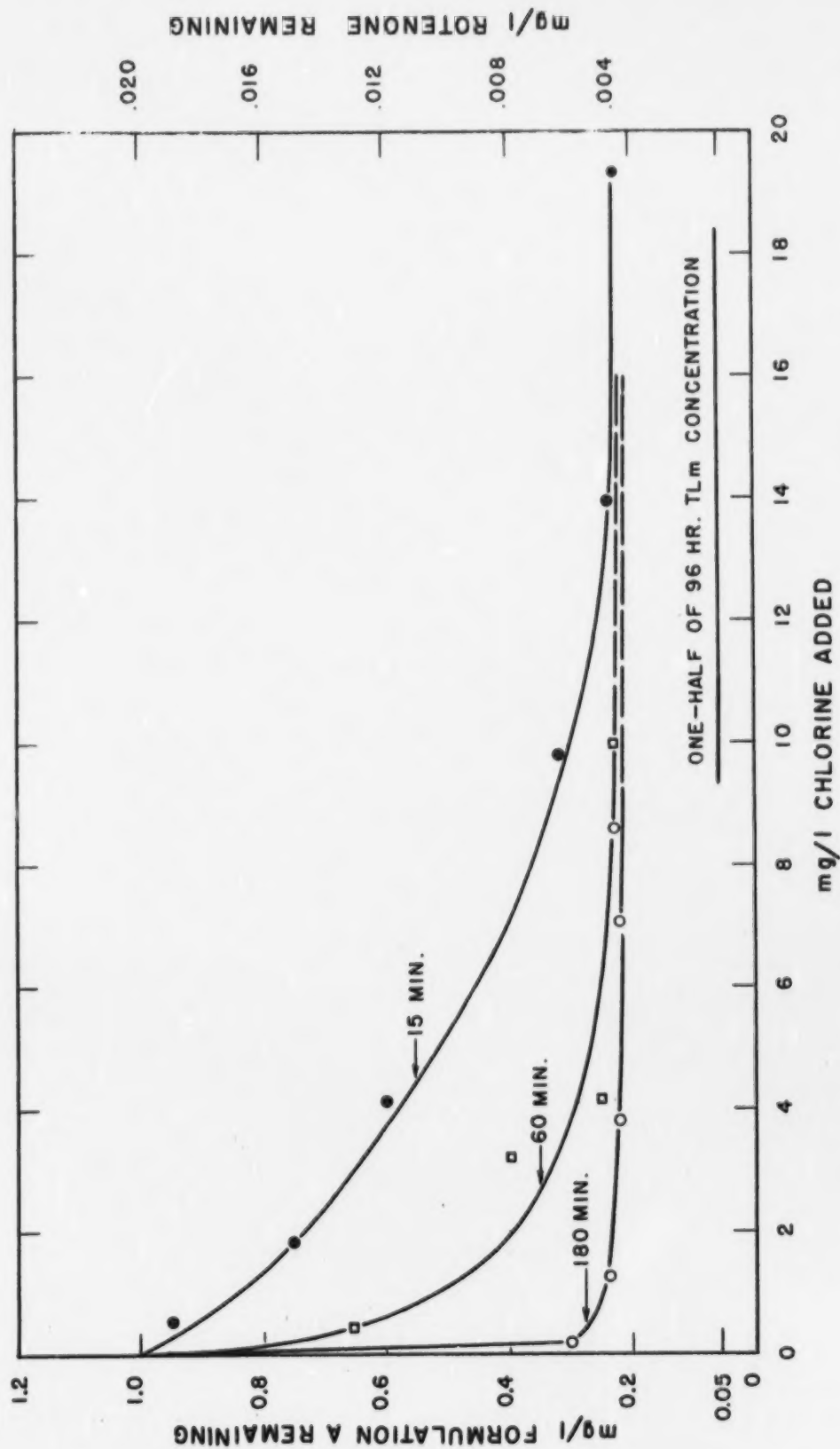


CARBON DOSAGE CHART FOR REMOVAL OF FISH POISONS



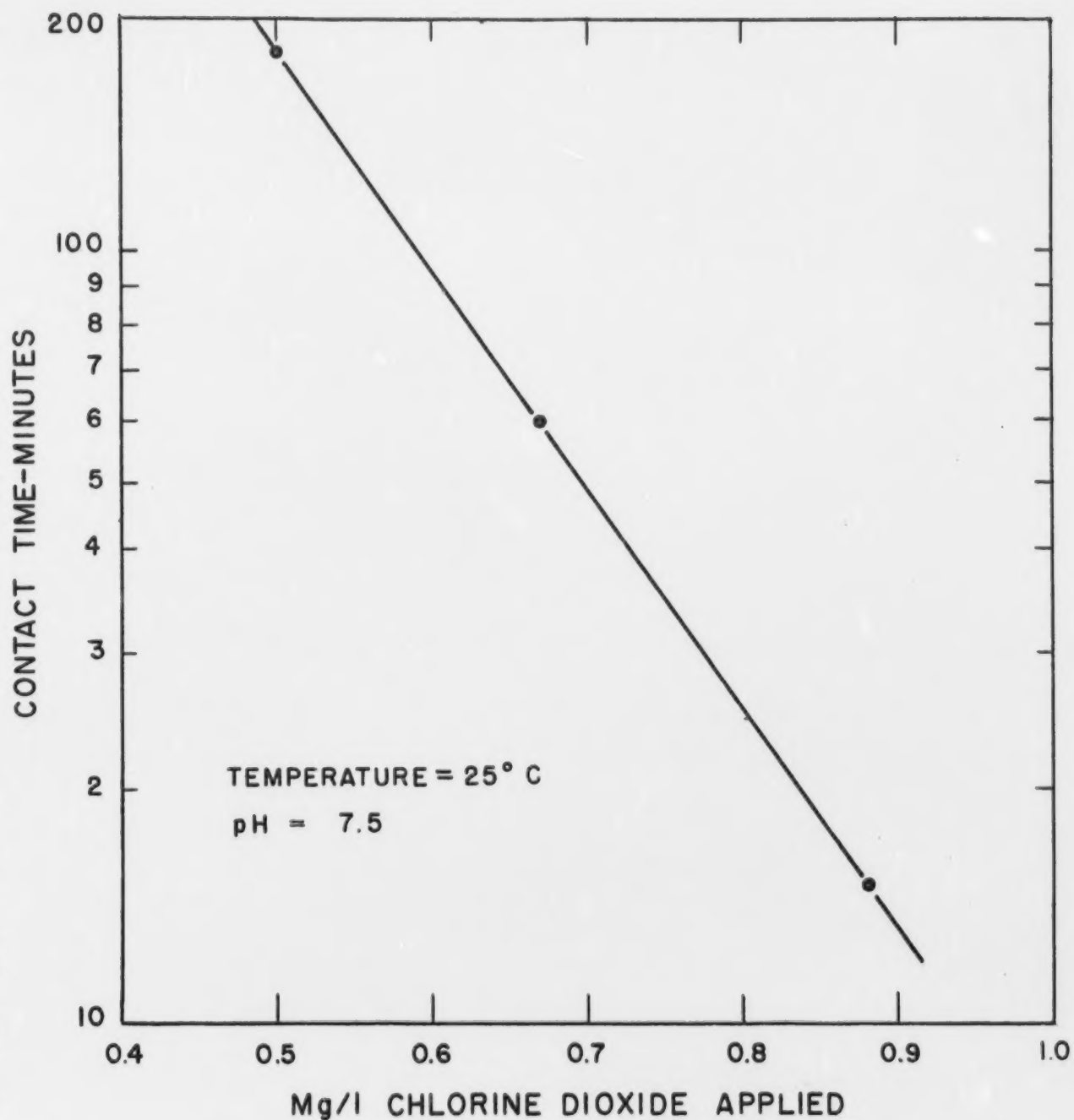
CHLORINE TREATMENT OF 0.1 Mg/l ROTENONE SOLUTION

FIGURE 5



CHLORINE TREATMENT OF 1.0 mg/l OF FORMULATION
A FOR VARIOUS CONTACT TIMES

FIGURE 6



RELATIONSHIP OF CONTACT TIME AND
CHLORINE DIOXIDE REQUIRED TO DETOXYFY
0.1 Mg/l ROTENONE

FIGURE 7

EFFECT OF FISH POISONS ON WATER SUPPLIES

II. ODOR PROBLEMS

by

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September, 1959

U. S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE

Public Health Service

EFFECT OF FISH POISONS ON WATER SUPPLIES

II. Odor Problems

INTRODUCTION

(1)

In a previous paper the problems of treating water containing a fish poison were discussed and data were presented on the ability of various water treatment processes to remove the toxic agents deliberately added to a water during fish management operations. This paper reports the results of experiments aimed at assessing the odor potential of various fish poison formulations and the ability of water treatment processes to remove these odors.

MATERIALS

Pure rotenone or toxaphene, currently the principal toxic agents, are practically never used in fish management operations. For ease of handling and to enable effective dispersion, these toxic materials are invariably formulated with other materials which include synergists, solvents, emulsifiers, or clay carriers. Hence, in addition to the materials previously studied, selected solvents were also investigated. Compounds studied are listed in Table I.

TABLE I
FISH POISONS AND COMPONENTS
INVESTIGATED

Material	Rotenoids	Toxaphene	Synergist	Solvent	Emulsifier	Clay
Formulation A	X	X		X	X	X
Formulation B	X			X	X	
Formulation C	X		X	X	X	
Formulation D	X			X	X	
Rotenone	X					
Toxaphene		X				
Sulfoxide			X			
Aerosol OT					X	
Solvent #1				X		
Solvent #2				X		
Solvent #3				X		
Deodorized Kerosene				X		

METHODS

One of the fish poison formulations, D, was studied in detail. In addition to a determination of threshold odor concentration of the material itself, removal from water was attempted by several water treatment processes which included activated carbon adsorption, alum coagulation, and chlorination. In each of these studies, effectiveness of removal was judged by determination of odor reduction. Results from the detailed study of this particular formulation quickly demonstrated that the only effective means for odor removal was treatment with activated carbon. Therefore, only this treatment process was applied to the other formulations and fish poisons. Some of the materials, because of their high threshold odor concentrations, were not studied for removal since they would present no odor problems at water plants when used under normal practical conditions.

EXPERIMENTAL

THRESHOLD ODOR CONCENTRATION

The minimum amount of formulation or component which will produce a detectable odor was obtained by determining the threshold odor concentration. In this paper, the threshold odor concentration is defined as the smallest amount of material in aqueous solution or emulsion whose odor is detected by 50% of the test panel. The test and computations were made in the following manner.

A stock solution of a known concentration of material was prepared in odor-free Cincinnati tap water. In instances where solubility was exceeded, a fine emulsion was obtained by adding a solution of the material in isopropyl alcohol to the water and emulsifying in a Waring Blendor for 5 minutes. Addition of small amounts of isopropyl alcohol was shown not to interfere with the threshold odor concentration determination, and this method invariably produced a sufficiently stable emulsion. Successive serial dilutions by a factor of two were then made of the stock solution, and 200 ml portions were placed into 500 ml, glass-stoppered, odor-free Erlenmeyer flasks. This series of flasks containing decreasing amounts of material, along with blanks which contained only odor-free water, were appraised for the presence or absence of odor by a panel of eight individuals. Computation of the average threshold odor concentration was obtained by a moving average method.⁽²⁾ An illustration of this method is the determination of the threshold odor concentration of toxaphene, which is typical of all of the compounds tested.

A stock solution of toxaphene in isopropyl alcohol was added to 400 ml of odor-free tap water and emulsified in a Waring Blendor for 5 minutes. Successive two-fold dilutions were prepared and dispensed into glass-stoppered Erlenmeyer flasks and then submitted to a panel of observers.

Computation of the threshold odor concentration is shown in the Appendix. Threshold odor concentrations were determined on all of the pure compounds, formulations, and solvents listed in Table I. The data obtained, along with the computed 95% confidence limits, are shown in Table II.

Rotenone has a high threshold odor concentration but toxaphene with a threshold odor concentration of 0.005 mg/l would cause an odor problem in water. The very low threshold odor concentration of the commercial fish poison formulations tested, ranging from 0.007 to 0.023 mg/l, is due largely to the solvents which constitute up to 90% of the product.

The numbers and varieties of solvents available to the commercial formulators is so great that, for this study, only representative solvents could be studied. Proper selection of a solvent could yield a fish poison formulation that is practically odorless. It is evident that odor potential has received little or no attention in selecting the solvents currently being used in fish poison formulations.

REMOVAL BY ACTIVATED CARBON

The experimental methods used in studying the removal of contaminants by activated carbon have been fully described in a previous paper.⁽¹⁾ Briefly, a fixed concentration of contaminant was treated with varying amounts of activated carbon. After removal of the carbon by filtration

TABLE II
Threshold Odor Concentrations of
Fish Poison Formulations
and Components

Material	Threshold Odor Concentration mg/l	95% Confidence Limits	
		Upper	Lower
Formulation A	0.020	0.028	0.018
Formulation B	0.023	0.033	0.015
Formulation C	0.007	0.009	0.005
Formulation D	0.018	0.025	0.011
Cube Powder	30.6	41.6	24.0
Rotenone	13.8	23.1	9.6
Toxaphene	0.0052	0.010	0.0022
Sulfoxide	0.091	0.17	0.05
Aerosol OT	14.6	23.1	10.3
Solvent #1	0.016	0.021	0.004
Solvent #2	13.9	20.5	8.1
Solvent #3	0.090	0.143	0.057
Deodorized Kerosene	0.082	0.106	0.057

through a sintered glass filter, residual threshold odor number was determined by a panel of eight observers. From this the concentration of the contaminant is estimated by the formula:

$$\text{Concentration of Contaminant} = \frac{\text{TO Concentration}}{\text{TO number expressed as dilution factor}}$$

For example, toxaphene has a threshold odor concentration of 0.005 mg/l. After treatment of 2.0 mg/l of toxaphene with 10 mg/l of activated carbon, it was found that the treated water had a threshold odor number of 152. In other words, the sample had to be diluted 1-152 to obtain a non-odorous water. Expressed as a dilution factor, the threshold odor number becomes 0.0066. The concentration of chemical remaining in the water after carbon treatment is then obtained by the above expression.

$$\text{Concentration of Toxaphene} = \frac{0.005}{0.0066} = 0.76 \text{ mg/l}$$

Data obtained in this manner were used to construct carbon adsorption isotherms according to Freundlich's equation. Such isotherms were obtained for the pure fish poisons and solvents and for the fish poison formulations. Computations also were made for all of the compounds, using the parameters derived graphically from the adsorption isotherms, to determine the amount of carbon required to reduce any concentration of fish poison to a predetermined level.

(1)
This method of calculation was described in the previous paper.

Typical laboratory data for Formulation C, are shown in Table III, which, as shown in Table I, contains in addition to rotenone, a synergist and a highly odorous solvent. Also shown in Table III are the functions for the construction of an adsorption isotherm. The resulting carbon adsorption isotherm for Formulation C is shown in Figure 1. The considerable scatter of the individual points reflects the lack of precision in odor measurement. Notwithstanding the scatter, a line may be drawn which correlates adsorptive capacity per unit weight of carbon with concentration of adsorbate remaining in solution at equilibrium.

The parameters K and n in the Freundlich equation for this line were obtained graphically and then used to compute the amount of carbon needed to reduce any initial concentration of Formulation C to any desired level. The method of computation was described in the previous (1) paper. In Figure 2, two curves are shown which represent the desired residual odor following carbon treatment, the upper one depicting a residual TO number of 1 which is equivalent to a concentration of 0.0068 mg/l of Formulation C, the lower curve representing a residual TO number of 2, or a concentration of 0.0136 mg/l.

Carbon adsorption isotherms were obtained for all of the commercial fish poison formulations using odor measurement as a quantitative determination of residual chemical. These isotherms, Figure 3, show by their position and slope the intrinsic differences

TABLE III

Removal of Odor of Formulation C
by Activated Carbon Treatment

Carbon Added mg/l	Formulation C		Form. C Removed mg/l Carbon
	Remaining mg/l	Removed mg/l	
M	C	X	$\frac{X}{M}$
0.5	0.435	1.61	3.23
1.0	0.444	1.60	1.60
2.0	0.615	1.43	0.72
3.0	0.251	1.80	0.60
4.0	0.200	1.85	0.46
5.0	0.093	1.96	0.39
6.0	0.042	2.01	0.33
8.0	0.054	1.99	0.25
10.0	0.068	1.98	0.20
10.0	0.065	1.98	0.20
20.0	0.147	1.898	0.095
30.0	0.043	2.005	0.067
85.0	0.010	2.038	0.024

Initial Concentration of Formulation C = 2.048 mg/l

Threshold Odor Concentration of Formulation C = 0.0068 mg/l

in composition of the formulations. It should be pointed out here that an adsorption isotherm for a formulation is a composite of the individual isotherms of the several components. Isotherms for several of these components are shown in Figure 4.

No adsorption data by odor methods were obtained for rotenone which is the principal toxic agent in most fish poison formulations, since the threshold odor concentration is so high, 14 mg/l, that it would contribute no odor when applied in the normal concentration of field use.

The carbon adsorption isotherm of rotenone, as measured by bio-assay method, was, however, shown in the previous paper. ⁽¹⁾ For the same reason, no adsorption isotherm is shown for sulfoxide since the threshold odor concentration of this material, 0.091 mg/l, is greater than the concentration likely to be present in a water treated with any fish poison formulation. Treatment of a water with 2 mg/l of Formulation C would yield a concentration of 0.05 mg/l of sulfoxide.

These isotherms provided the data required to compute the curves shown in Figure 5. It is immediately apparent that a wide range exists between the easily adsorbed material to the difficultly adsorbed compounds. Formulation A, which contains the smallest amount of odorous hydrocarbon solvent, is most easily removed by carbon, only 36 mg/l being required to reduce the odor of 2.0 mg/l to a residual threshold odor number of 1. On the other hand, Formulation C, which is composed of 90% of a solvent which has a very low threshold odor concentration is the most difficult to remove and would require 85 mg/l of carbon.

OTHER METHODS OF TREATMENT

Other methods of treatment were used in the attempt to remove the odor of Formulation D. Application of chlorine up to 30 mg/l plus a contact time of 3 hours did not materially reduce the odor nor was the odor intensified by this application of chlorine.

A chlorine demand determination performed on a 2.0 mg/l aqueous emulsion of Formulation D showed no consumption of chlorine and, hence, by itself, Formulation D would not interfere with chlorination at a water plant.

PERSISTENCE OF ODOR

Because of the difficulty in reproducing field conditions in a laboratory no attempt was made to determine the persistence of the odor of all of the fish poison formulations under all conditions of environment. The persistence of the odor of Formulation D was studied to provide at least an idea of how long the odor problem would be troublesome where this compound is used.

An emulsion of 2.0 mg/l of Formulation D, prepared in odor-free tap water, was put into a wide-mouth gallon jar, covered loosely with a watch glass, and allowed to stand at laboratory room temperature. During the course of the experiment temperature ranged from 22 to 25° C. Samples for odor measurement were removed at intervals. The data in this experiment, Figure 6, showed that the odor of Formulation D is rapidly dissipated, within the first two days, with the rate considerably reduced thereafter.

After 7 days, 90% of the odor had disappeared from the solution with a threshold odor number of < 2 remaining.

DECOMPOSED FISH

EFFECTS

(3)

Hoffman and Payette, in their report on fish eradication in Hodges Reservoir, show that all fish killed by rotenone do not come immediately to the surface where they may be harvested. As long as 11 to 13 days after rotenone application, 64.2 tons of partially decomposed fish rose to the lake surface and were recovered. Delayed dead fish appearance has also been reported in other operations.

Since dead fish probably would remain in the water long enough for decomposition to occur, and since the odor of dead fish is repugnant to consumers, experiments were undertaken to determine the effectiveness of coagulation, carbon treatment, and chlorination in removing the odor.

An approximation of the amount of odor which might be encountered in practice was computed by assuming the worst conditions. To produce an odorous water, twenty fish which had been killed by rotenone, with a total weight of 24 grams, were put into 20 liters of test water and allowed to stand for two days at room temperature of 21° C. The decomposed fish were removed, and the odorous water was then stored at 1° to 2° C.

A quantitative measurement of the odorous water was obtained by a standard threshold odor determination and by a 30-minute chlorine demand determination. The threshold odor number, using a panel of four subjects, was found to be 2048. Determination of chlorine demand revealed that a classical type of curve is obtained (Figure 7). The 30-minute total chlorine demand was 68 mg/l. The sharp "break" may be attributed to the presence of ammonia and amines, especially trimethylamine, which are frequently associated with decomposing fish.⁽⁴⁾

TREATMENT

Alum Coagulation

Effectiveness of alum coagulation in removing odor and chlorine demand compounds of decomposed fish in water was determined by coagulating, with varying amounts of alum, a solution containing 10% by volume of odorous water. Both odor and chlorine demand determinations were performed on the effluents. Water which had been treated with 90 mg/l of alum produced an effluent with a threshold odor number of 128 and a chlorine demand of 6.5. These values correspond fairly closely to a simple 1 to 10 dilution of the odorous water, which would give values of 205 and 6.8 for threshold odor number and chlorine demand respectively. Alum coagulation alone, therefore, has no significant effect on either odor or chlorine demand and will not produce a palatable effluent.

Carbon Treatment

Odor removal by activated carbon was checked by adding increasing amounts of carbon to a 5% by volume solution of odorous water. As in the previous tests, threshold odor number and chlorine demand determinations were made on the effluents.

Treatment with 40 mg/l of carbon completely removed all of the odor. A threshold odor number of 2 was obtained with 30 mg/l of carbon. Significantly, the chlorine demand of the effluents was not materially reduced. These results would indicate that the odor of the decomposed fish was due to protein decomposition products other than amines and ammonia. These latter compounds apparently resist carbon adsorption and appear in the effluent as chlorine demand even after treatment with carbon.

Chlorine Treatment

A further test was made on the effect of varying doses of chlorine, in concentrations below and above the chlorine demand value. Amounts of chlorine ranging from 0.9 to 4.6 mg/l were added to a 5% solution by volume of odorous water. Dilution of the odorous water to 5% yields a threshold odor number of 10, and a chlorine demand of 3.4 mg/l. The results show that the odor producing compounds are readily destroyed by small amounts of chlorine; 1.8 mg/l of chlorine produced an effluent with a threshold odor number of 1 and 4.6 mg/l of chlorine provided an odor free effluent.

No estimate is available on the intensity of the odor which may appear in a water following fish poison application. Certainly, field conditions will determine the numbers of fish which will evade harvesting. However, it is clear from the experimental work that odor produced by decomposing fish can be removed by activated carbon or by free residual chlorination.

DISCUSSION

Presence of fish poison formulation in a water supply poses two basic problems to a water treatment plant; that of removal of the toxic component, and that of reduction of odor to a level of potability. Of the two, the latter problem is the one more likely to prove troublesome to the water plant since toxicity of fish poisons is removed by much smaller doses of carbon than is required to remove odor.

Data in Tables II and IV reveal the significant fact that almost all of the odor in fish poison formulations, with the exception of the one containing toxaphene, is due to the solvent content. Removal of the odor due to the solvent also requires the major portion of carbon needed for odor reduction of the formulation. For example, Solvent #1, with a threshold odor concentration of 0.016 mg/l, comprises almost the entire odor material in Formulation D, which has a threshold odor concentration of 0.018 mg/l. To remove this odorous solvent contained in 2.0 mg/l of Formulation D requires 62 mg/l of carbon, while 50 mg/l are required to remove the odor of the solvent without the presence of the active materials.

The difference in carbon requirement may be ascribed to the presence of emulsifier and rotenoid compounds which could affect the carbon adsorption to this degree.

While the types of solvents currently in use in fish poison formulations have undoubtedly met all of the manufacturer's requirements of low cost, solubility of rotenoids and emulsifiers, ease of application and successful dispersion, this study has uncovered serious disadvantages in the use of the present formulations in water supply reservoirs. Application of 2.0 mg/l of any of the formulations tested renders a water unpalatable and requires treatment with up to 85 mg/l of activated carbon to produce potable water. Further, while odor may be successfully reduced with activated carbon, no information exists on the removal of unknown, and possibly dangerous, materials from the solvent. These solvents are derived from the distillation of petroleum and coal tar crudes and their exact composition is not known. Addition of materials of unknown composition to a water supply is not a good practice.

For the above reasons, it would be desirable that a more suitable solvent be developed for use in fish poison formulations intended for application to water supply reservoirs. In addition to the usual requirements for a solvent demanded by the manufacturer or user, other desirable characteristics would be: (a) high threshold odor concentration (the solvent should produce little or no odor when suspended or dissolved in water in a concentration of 2.0 mg/l); (b) non-toxic to humans and

TABLE IV

Carbon Requirements for Removal of
Toxicity and Odor Caused by
Fish Poisons

Compound	Initial Conc. mg/l	Carbon Required mg/l	
		Fish (a) Toxicity	(b) Odor
Rotenone	0.1	6.6	Non-odorous ^(c)
Toxaphene	0.1	5.0	5.0
Cube Powder	2.0	9.8	Non-odorous ^(c)
Formulation A	2.0	8.8	36
Formulation B	2.0	26.4	78
Formulation C	2.0	21.6	85
Formulation D	2.0	16.7	62
Solvent #1	2.0	Non-toxic ^(d)	50
Deodorized Kerosene	2.0	Non-toxic ^(d)	52

- (a) Concentration of carbon required to reduce compound to one-half of 96-hour TL_m value. These data obtained from previous publication (1).
- (b) Concentration of carbon required to reduce odor of compound to a threshold odor number of one.
- (c) Material is non-odorous in the concentrations normally used.
- (d) Material is non-toxic to fish in the concentrations normally used.

other mammals; (c) of known composition; and (d) readily dissipated by natural and biological agencies after dispersion in a water. These characteristics are met by such solvents as acetone or isopropyl alcohol. Certainly, other solvents are available which could meet these requirements.

SUMMARY

Odor in a raw water supply following contamination with the fish poisons tested may be removed effectively by activated carbon. No other common water treatment process will successfully reduce the odor of 2.0 mg/l of fish poison formulation to acceptable levels. The doses of carbon required for the formulations tested in this study varied from 36 to 85 mg/l. Such carbon dosages are unusually large and would be a serious economic burden for the routine treatment of water. However, since fish poison formulations would be applied infrequently and since the odor of most of the formulations persists for only a short time, during which interval decreasing dosages of carbon are required, the increased cost of water treatment may not be very large. Use of formulations containing toxaphene would require sustained treatment with carbon because of the high stability of toxaphene.

Because of the unusual odor problem and unknown composition of the solvents presently used in fish poison formulations, it is recommended that a more suitable solvent be developed for use in formulations intended for water supply application.

It must be emphasized that since fish poison formulations are subject to changes at the discretion of the manufacturer, the data reported in this paper are valid only for the samples tested.

ACKNOWLEDGMENT

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COMPUTATION OF THRESHOLD ODOR CONCENTRATION OF TOXAPHENE

Results of the panel observations for the various concentrations of toxaphene are shown in Table A. Computations of the threshold odor concentration are then made by tabulating the data as shown in Table B.

In column I of Table B, the concentrations that the panel is subjected to are listed in decreasing order. The log of these concentrations are tabulated in column II. In column III the percentage of positive results obtained by the panel members for each concentration tested are listed in decimal form. In the fourth column the angles corresponding to the percentage positive results obtained for any given concentration are listed. A table for transforming percentages to degrees (5) is given by Fisher and Yates, Table XII. In the fifth column the moving average of the angles listed are taken over a span of three angles.

The value of the threshold odor concentration is then given by the following equation.

$$\text{Equation 1. } \log \text{ TO conc.} = X_i + (X_{i+1} - X_i) \left[\frac{45 - Y_i}{Y_{i+1} - Y_i} \right] \text{ where}$$

Y_i is the moving average which is equal to or just less than 45° . The log concentration corresponding to this moving average is termed X_i . The moving average in degrees which is just greater than 45° is denoted by Y_{i+1} . The corresponding log concentration is called X_{i+1} . Thus, in the above example:

$$Y_i = 40^\circ$$

$$Y_{i+1} = 53^\circ$$

$$X_i = 0.6021$$

$$X_{i+1} = 0.9031$$

The log of the TO concentration is then given by the following:

$$\log \text{ TO conc.} = 0.6021 + (0.9031 - 0.6021) \left[\frac{45 - 40}{53 - 40} \right]$$

$$\log \text{ TO conc.} = 0.7178$$

The antilog of the TO concentration is then equal to the threshold odor concentration. For toxaphene this value is 0.0052 mg/l.

An extension of this method of calculating the average TO concentration may be used to compute 95% confidence limits for the true threshold odor, i.e., limits which will, with a probability of .95, include the true TO value.

The formulas given below represent an extension of results obtained by Bennett and have been published in more general form by Harris. (2) (6)

The following expressions are required:

$$\text{Equation 2. } A = \frac{45 - Y_1}{Y_1 + 1 - Y_1} = \frac{X}{Y}$$

$$\text{Equation 3. } \text{Variance of } Y = \frac{2 \times 820.7}{9 \times n} \text{ where } n = \text{size of panel.}$$

$$\text{Equation 4. } g = \frac{(1.96)^2 \times \text{Variance } Y}{Y^2}; g \text{ must lie between 0 and 1.}$$

$$\text{Equation 5. } A - \frac{g}{2} + \frac{\sqrt{g}}{1 - g} \sqrt{(A - 1/2)^2 + (1 - g) \cdot \frac{5}{4}}$$

Denoting the smaller number in Equation 5 by A_1 and the larger number by A_2 , the 95% confidence limits for the log TO concentration are given by:

$$\text{Equation 6. } \text{Lower confidence limit} = L_1 = X_1 + (X_1 + 1 - X_1) A_1$$

$$\text{Equation 7. } \text{Upper confidence limit} = L_2 = X_1 + (X_1 + 1 - X_1) A_2$$

The 95% confidence limits for the true TO concentration are obtained by taking the antilogs of L_1 and L_2 . In the example shown for toxaphene these computations lead to 0.0022 and 0.0104 mg/l.

TABLE A

Determination of Threshold Odor Concentration of Toxaphene

Concentration µg/l	Panel Observations							
	1	2	3	4	5	6	7	8
128	+	+	+	+	+	+	+	+
64	+	+	+	+	-	+	+	+
Blank	-	-	-	-	-	-	-	-
32	+	+	+	+	+	+	+	+
16	-	+	+	+	+	+	+	+
8	-	+	+	+	-	+	+	-
Blank	-	-	-	-	-	-	-	-
4	-	+	+	+	-	+	-	-
2	-	+	-	-	-	+	-	-
1	-	+	-	-	-	+	-	-
0.5	-	-	-	-	-	-	-	-
0.25	-	-	-	-	-	-	-	-

TABLE B

Computations of the Threshold Odor Concentration of Toxaphene

I	II	III	IV	V
Concentration Tested - $\mu\text{g/l}$	Log. of Concentration	Proportion Positive	Angle	Moving Average Angle
128	2.1072	1.000	80°^*	-
64	1.8062	0.875	70°	76.7
32	1.5052	1.000	80°^*	73.3
16	1.2041	0.875	70°	67.3
8	0.9031	0.625	52°	53.3
4	0.5021	0.375	38°	40.0
2	0.3010	0.250	30°	32.7
1	0	0.250	30°	23.3
0.5	-.3010	0	10°^*	16.7
0.25	-.6021	0	10°^*	-

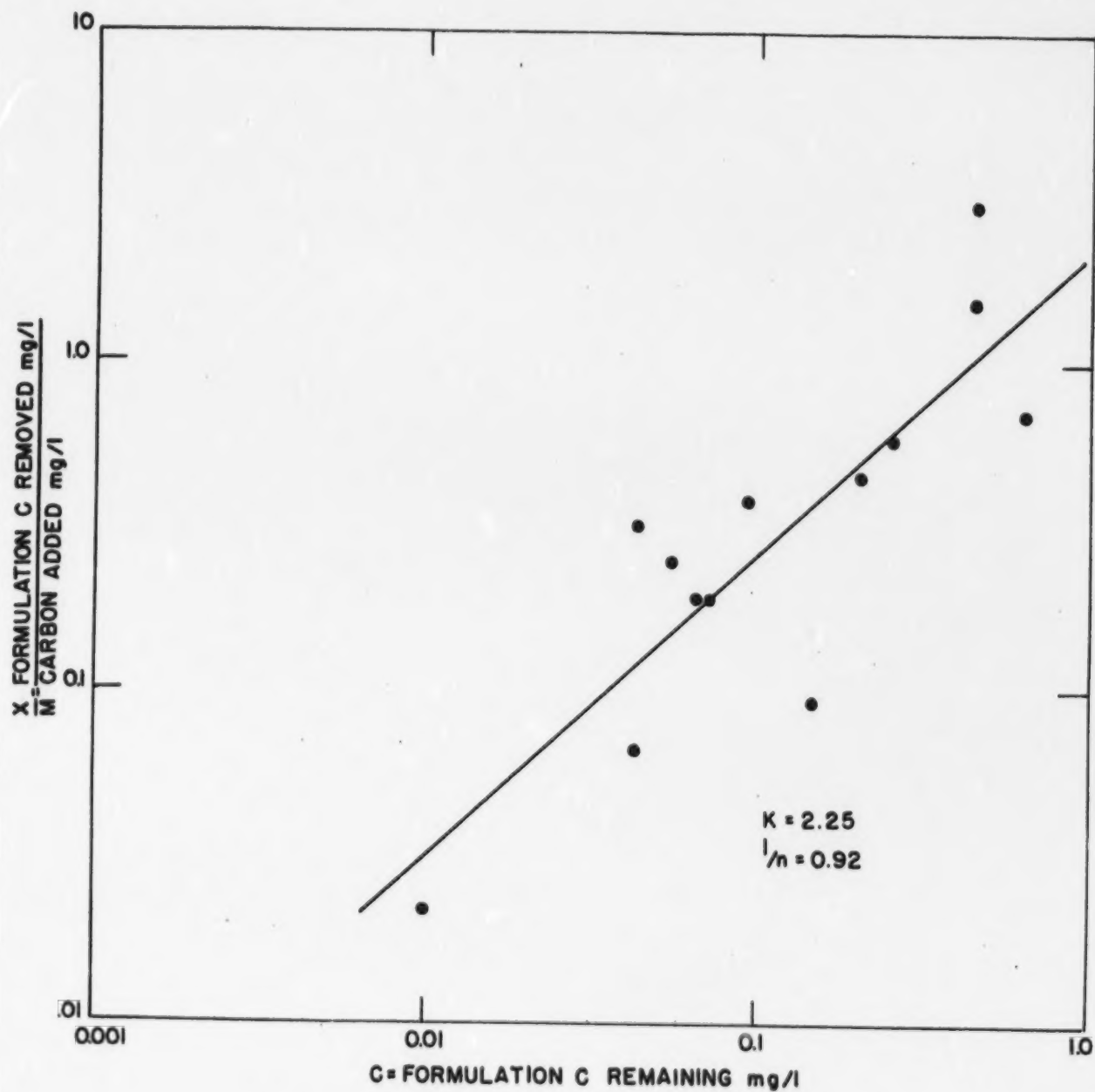
* For 0% response, the proper angle is $\arcsin \sqrt{\frac{1}{4n}}$

For 100% response, the proper angle is $90 - \arcsin \sqrt{\frac{1}{4n}}$

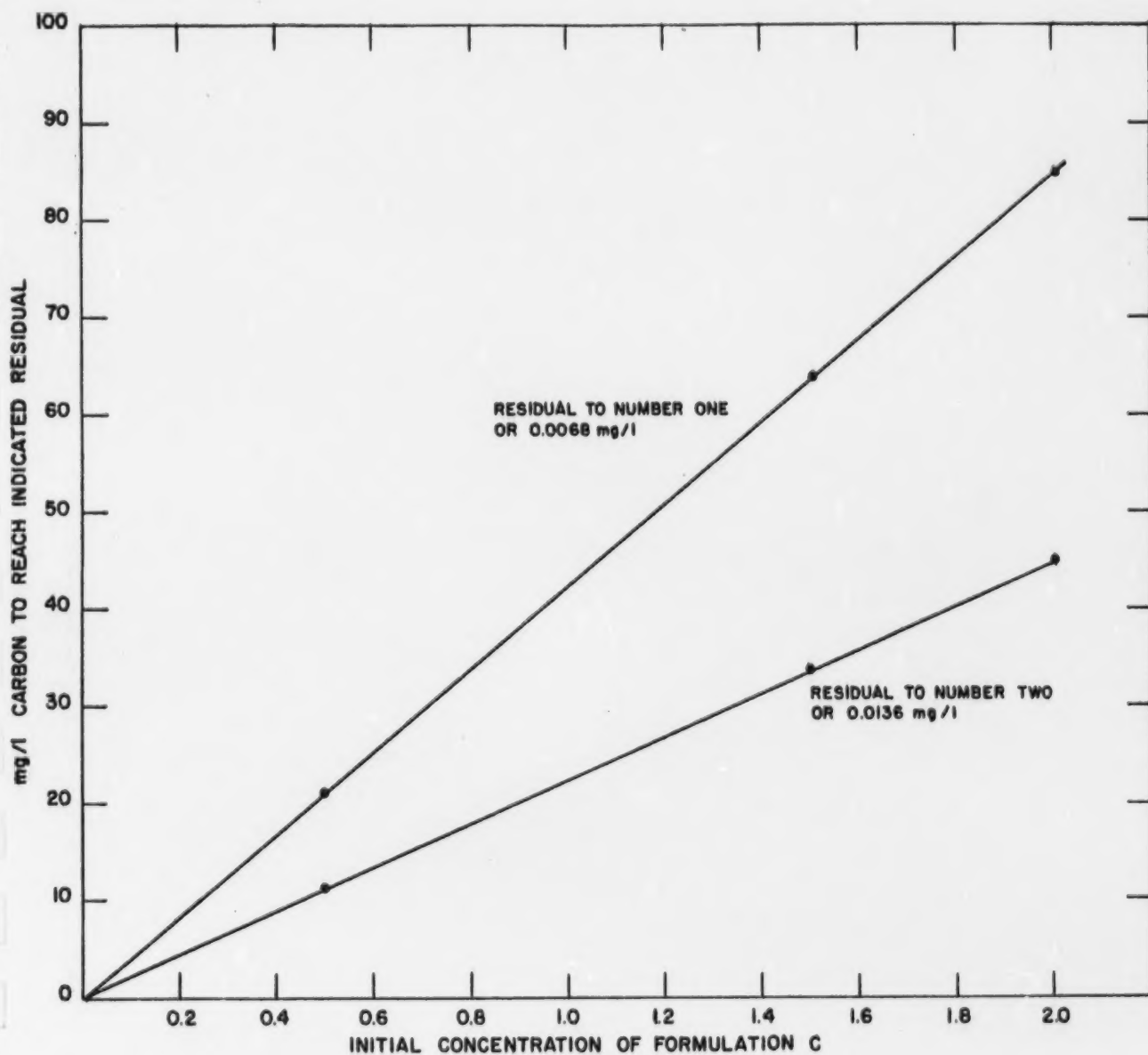
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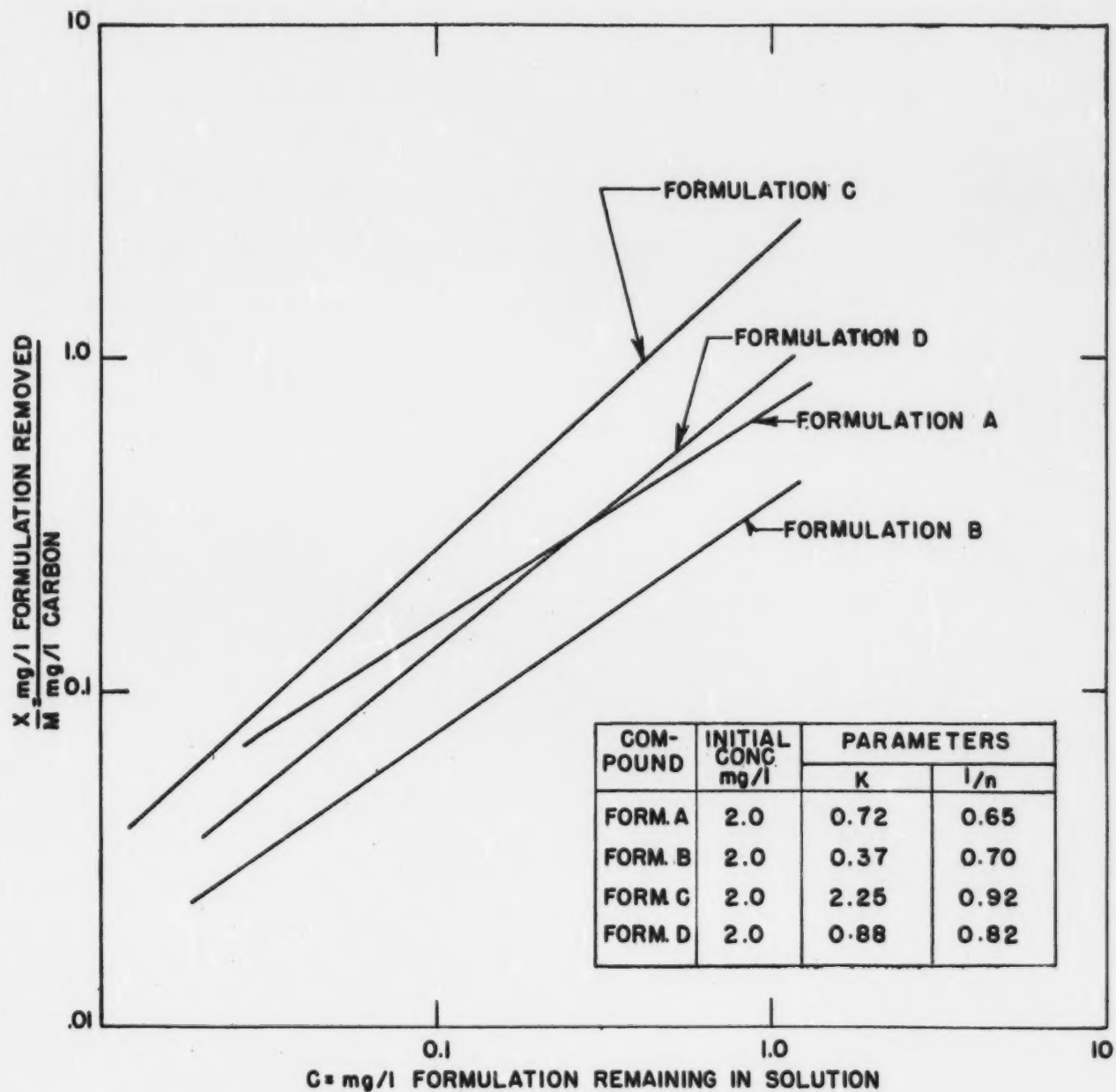


CARBON ADSORPTION ISOTHERM
FOR FORMULATION C
FIGURE 1



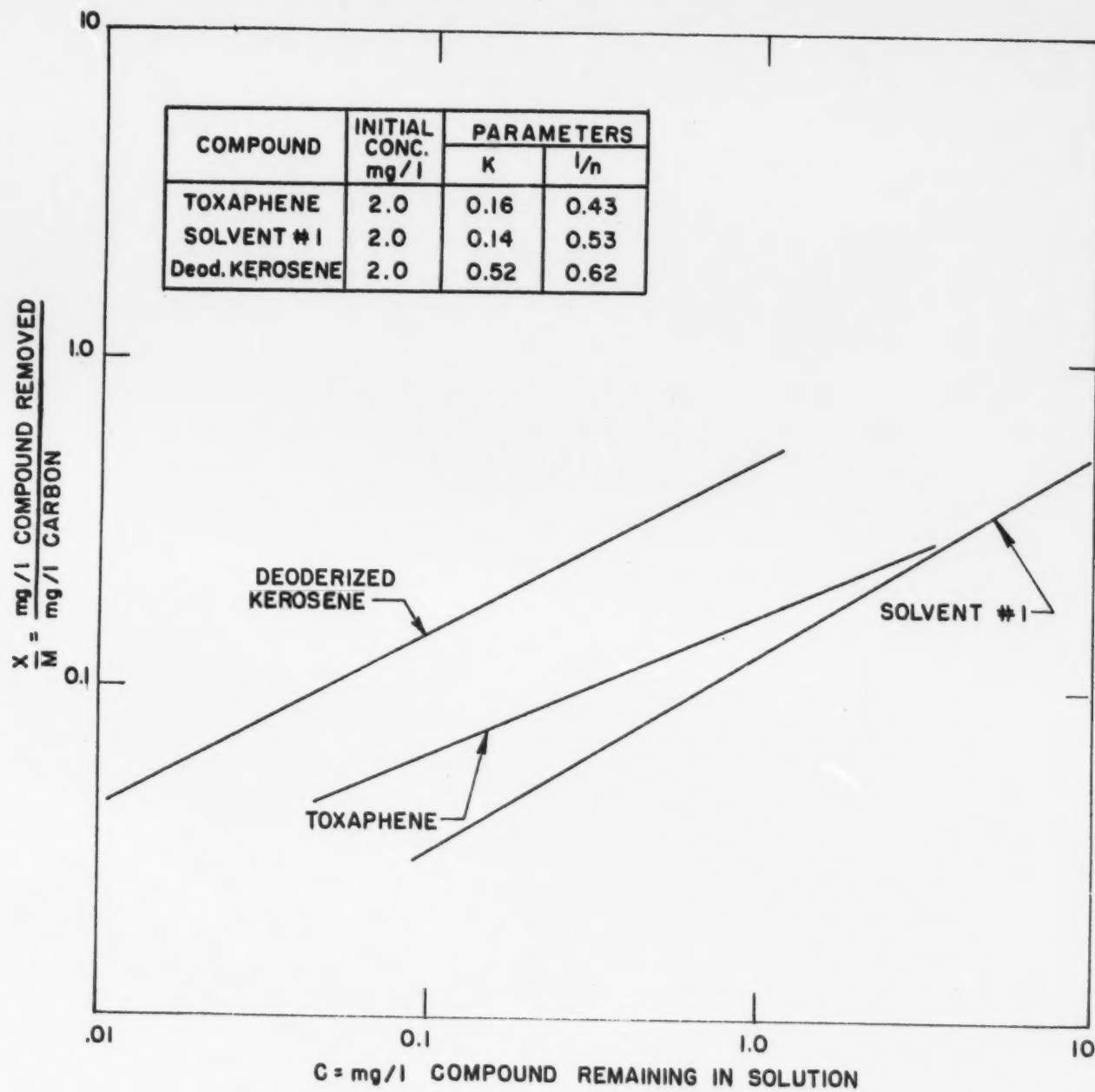
CARBON DOSAGE CHART FOR REMOVAL
OF FORMULATION C

FIGURE 2



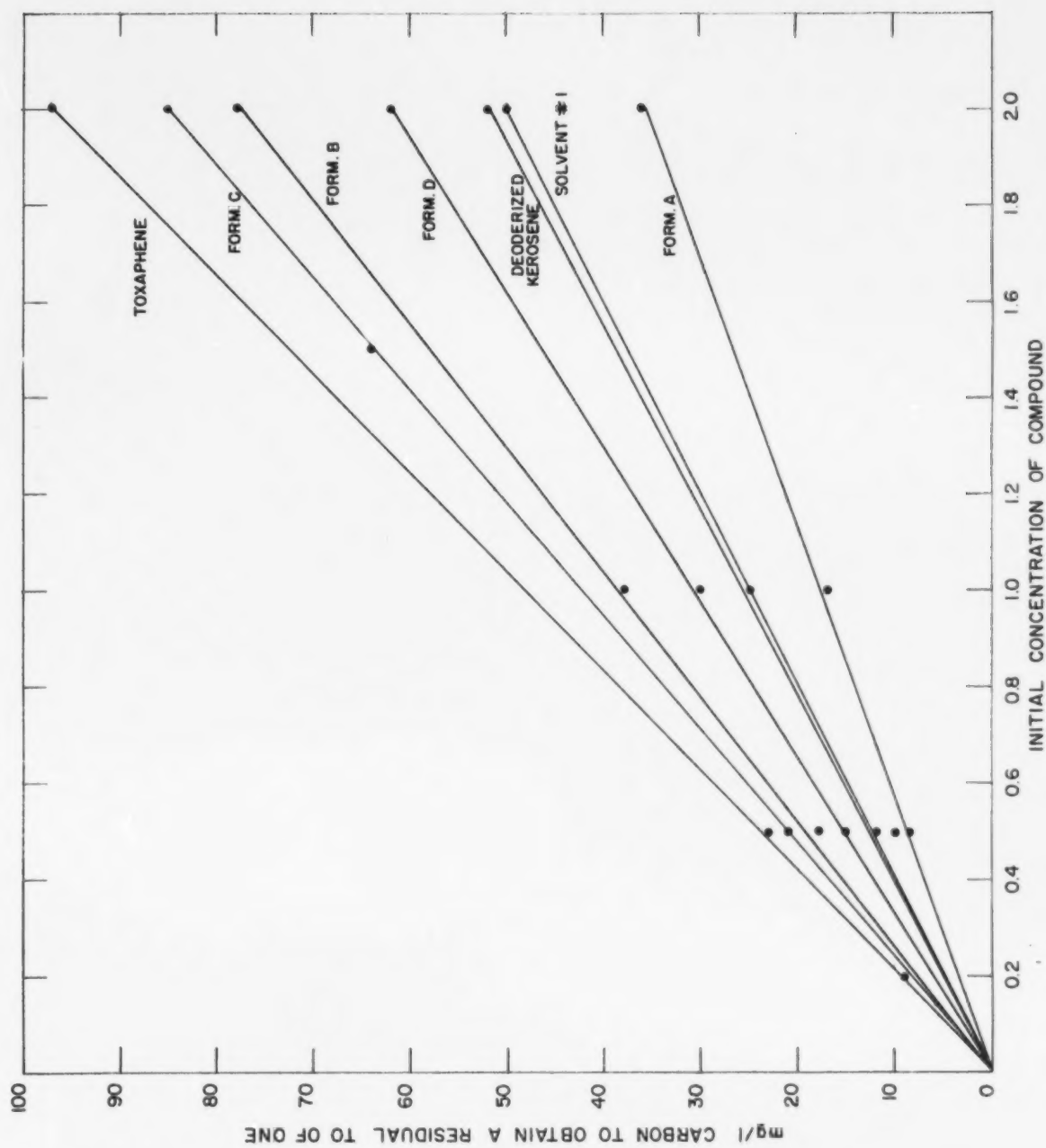
CARBON ADSORPTION ISOTHERMS FOR
COMMERCIAL FISH POISON FORMULATIONS

FIGURE 3

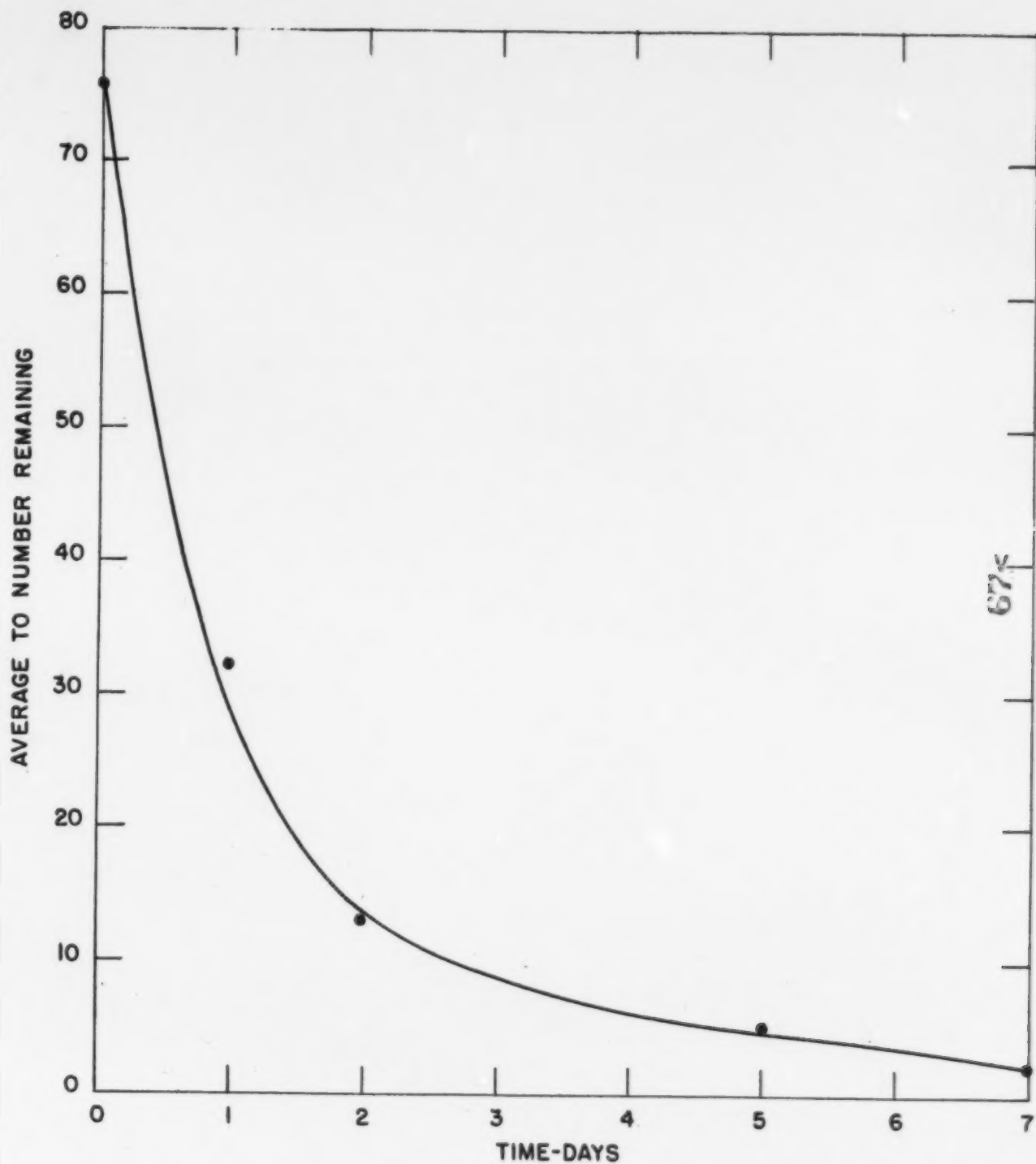


CARBON ADSORPTION ISOTHERMS FOR
FISH POISON COMPONENTS

FIGURE 4

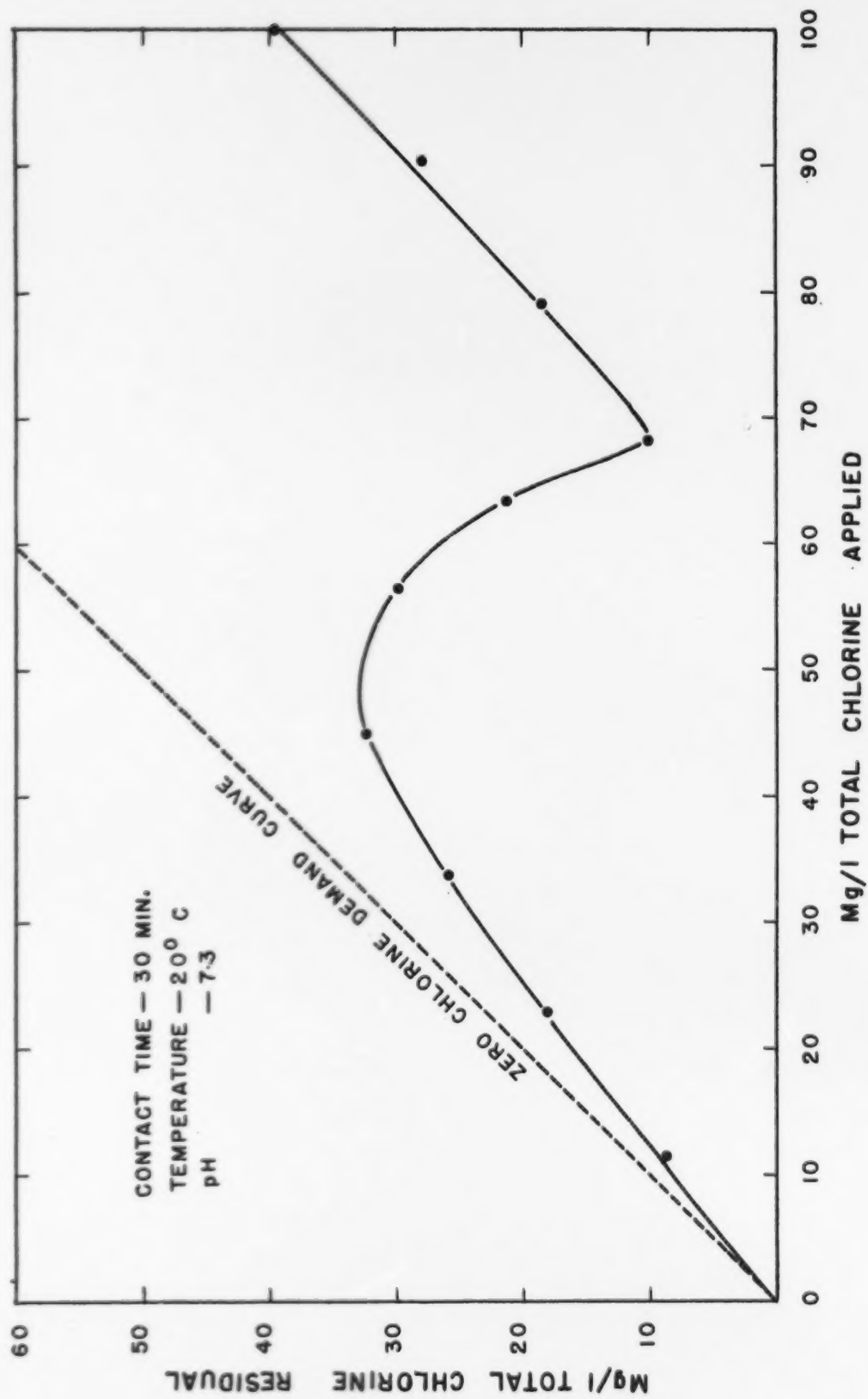


CARBON DOSAGE CHART FOR REMOVAL
OF FISH POISON COMPOUNDS AND COMPONENTS
FIGURE 5



REDUCTION OF THRESHOLD ODOR NUMBER OF 2.0 mg/l
EMULSION OF FORM. D ON STANDING AT ROOM TEMP.

FIGURE 6



CHLORINE DEMAND OF ODOROUS WATER

FIGURE 7

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EFFECT OF FISH POISONS ON WATER SUPPLIES
III. FIELD STUDY - DICKINSON, NORTH DAKOTA

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September, 1959

U. S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE

Public Health Service

EFFECT OF FISH POISONS ON WATER SUPPLIES

III. Field Study - Dickinson, North Dakota

INTRODUCTION

Because of the large coarse fish population in the Dickinson Reservoir, the North Dakota State Game and Fish Department proposed treatment of the lake with a rotenone preparation to eradicate the existing fish population. Since the Dickinson Reservoir was the raw water supply for the City of Dickinson, approval was requested from the North Dakota State Department of Health which asked for advice from the Public Health Service.

Studies were undertaken at the Robert A. Taft Sanitary Engineering Center to determine the feasibility of treating water which had been contaminated with a fish poison. The results of these studies have been reported in this Journal. (1)(2)

These investigations showed that both toxicity and odor produced by the presence of fish poison formulations in raw water supplies can be reduced to safe and palatable levels by treating with activated carbon in a water treatment plant. Data were also

obtained which demonstrated that the duration of the problem at the water plant would be relatively short since both rotenone and solvent are largely dissipated within one week.

On the basis of the results of these studies approval for the Dickinson Reservoir fish eradication project was granted to the State Game and Fish Department by the North Dakota State Department of Health. Request was made for the Public Health Service to have an observer at Dickinson who could assist in evaluating the treatment of the water during the operation.

FISH ERADICATION PROGRAM

The fish killing operation was conducted by the State Game and Fish Department. On August 26, 1958 Dickinson reservoir and influent streams were treated with a total of 5,500 gallons of Pro-Noxfish.^{*} Dickinson Reservoir is an impoundment of the Heart River with a surface area of about 800 acres and a volume of approximately 5,800 acre feet. To aid in the uniform distribution of the fish poison, the lake was sectioned as shown in Figure 1, and quantities of poison, calculated to produce a concentration of 2.0 mg/l, were apportioned to each section.

^{*}Trademark of S. B. Penick & Company. Contains 2.5% rotenone, 5% cubé and derris root extractives, 2.5% sulfoxide and 90% inerts.

The chemical was applied by spraying from boats equipped with a motor driven pump, a 55-gallon drum containing the toxicant and two discharge spray nozzles. Rapid operation of the boats repeatedly over the surface of the lake helped to emulsify and distribute the chemical. Shallow areas of the lake and tributary streams were treated by hand spraying.

Within a half-hour of the application of the poison, fish appeared on the surface. By mid-afternoon, when the toxicant had been applied to the main part of the lake, the crew started to harvest the floating fish. Poisoning of the tributary streams was continued for an additional day. The harvested fish consisted largely of carp, suckers, bullheads, and small bluegills. A limited number of game fish **also** were harvested. Practically all of the visible dead fish were removed from the lake and trucked to a rendering plant. Fish continued to appear on the surface of the lake in large amounts for the next two days and in lesser amounts for several days thereafter. It is estimated that 70 tons of dead fish were recovered. The lake was restocked with game fish in the spring of 1959.

WATER TREATMENT PLANT

The water supply for the City of Dickinson, population about 8,000, is obtained from the Dickinson Reservoir. The water intake is located at a depth of approximately 15 feet of water near the

concrete dam, and the water flows by gravity through a 16-inch conduit for a distance of 6,840 feet until it enters the water treatment plant. A schematic diagram of the water treatment plant is shown in Figure 2. Treatment capacity of the water plant is 2 MGD. In addition to the surface supply, wells are available which can produce 0.8 MGD. Storage capacity of about 1.3 million gallons is provided in the distribution system.

Facilities are provided at the raw water intake adequate for free residual chlorination. Three dry chemical feeders serve to add alum, lime, and activated carbon. A small pump adds liquid hydrofluorosilic acid directly to the Accelerator^{*}. Water leaving the Accelerator is treated with a polyphosphate compound for corrosion control. Recarbonation facilities are provided but were not operating during the fish killing operation. The standard rapid sand filters were operated at the rate of 2.5 gallons per square foot per minute. Facilities for post chlorination are also available at the clear well.

Since the existing chemical feeder for activated carbon could feed a maximum of only 10 mg/l, an additional feeder which could supply the required 60 mg/l of carbon was improvised. The auxiliary feeder consisted of a 55-gallon steel drum which was equipped with

^{*}Infilco, Inc.

a mechanical stirrer and with an outlet controlled by a valve located at the bottom of the drum. The feeder was located astride an open channel carrying raw chlorinated water to the Accelerator. The valve was adjusted to deliver at the rate of 50 gallons of carbon slurry in two hours. The amount of carbon fed to the coagulation tank was controlled by varying the amounts of carbon added to the drum.

LABORATORY CONTROL

In addition to the normal control tests two types of determinations were made for control of the water treatment; quantitative analysis of the toxic component in both the raw and finished water by fish bioassay and determination of threshold odor number of the raw and finished waters. Additional samples were also obtained from the lake at various points and depths to assess the distribution of toxicant and from several points in the water distribution system.

Three pairs of carbon filters were installed and operated to obtain an estimate of the extractable organic material in the raw and finished waters before, during, and after the fish killing project.

DETERMINATION OF TREATMENT DOSAGE

Before the fish kill operation had started, laboratory studies were made to determine the dosage of activated carbon which would be required to produce safe and palatable water. The methods used were (1)(2) described in the previous publications. A fixed concentration of Pro-Noxfish (the fish poison formulation which would be used in the lake) was added to the test water and was then treated with increasing amounts of activated carbon. Degree of removal of toxicant and odor was determined by fish bioassay and threshold odor number respectively. The data were used to plot carbon adsorption isotherms according to the Freundlich equation which then allowed the computation of the carbon dosages which would be required to reduce any concentration of fish poison to any desired level. These data are shown in Table I and the resulting carbon adsorption isotherms are shown in Figure 3. The parameters derived graphically from these curves, were then used to compute the carbon dosages required to reduce any initial concentration of Pro-Noxfish to the desired residual. These curves are shown in Figure 4. For fish toxicity the permissible residue was taken as one-half of the 96-hour TL_m value as described in the (1) previous publication. A threshold odor number of one was chosen as the desired residual odor. These values are equivalent to 0.03 and 0.013 mg/l of Pro-Noxfish respectively remaining in solution following carbon treatment. It is immediately apparent from Figure 4, that

treatment with activated carbon with sufficient amounts to remove odor would always result in the concurrent removal of fish toxicity with more than adequate overdose of carbon. These laboratory data demonstrated that a minimum of 59 mg/l of carbon would have to be added at the water treatment plant to reduce the odor of 2.0 mg/l of Pro-Noxfish to a residual threshold odor number of one. Only 21 mg/l of carbon would be needed to reduce the toxicity of 2.0 mg/l of Pro-Noxfish to one-half of the 96-hour TL_m value.

WATER TREATMENT

At 6:30 a.m., on August 26, 1958, treatment of Dickinson Reservoir with Pro-Noxfish was started. At the treatment plant, water was being supplied to the distribution system from the wells by operating them at their capacity rate of 0.8 MGD and from storage which had been filled the previous night to their capacity of 1.3 million gallons. In the meantime water from the water treatment plant was diverted to waste until a determination of the concentration of Pro-Noxfish in the raw water, both by fish bioassay and by odor value, could be made. The first three samples of raw water contained an average of 2.0 mg/l of Pro-Noxfish as determined by bioassay and had an average threshold odor number of 40. According to Figure 4, 59 mg/l of activated carbon would be needed to reduce this concentration to a safe and palatable level.

TABLE I
ACTIVATED CARBON TREATMENT OF
EMULSION OF PRO-NOXFISH

Carbon, Added mg/l	(a)			FISH TOXICITY ^(b)		
	ODOR					
	Removed	Remain		Removed	Remain	
11	X	C	$\frac{X}{M}$	X	C	$\frac{X}{M}$
Expressed as Mg/l Pro-Noxfish						
2	-	-	-	0.75	1.25	0.38
4	-	-	-	1.40	0.60	0.35
5	0.99	1.06	0.198	-	-	-
6	-	-	-	1.62	0.38	0.27
8	-	-	-	1.81	0.19	0.23
10	1.74	0.31	0.174	1.85	0.15	0.19
15	1.74	0.31	0.116	-	-	-
21	2.00	0.05	0.095	-	-	-
30	2.01	0.04	0.067	-	-	-
40	2.02	0.03	0.051	-	-	-
75	>2.04	<0.01	-	-	-	-

(a)

Initial concentration of Pro-Noxfish = 2.05 mg/l.

(b)

Initial concentration of Pro-Noxfish = 2.0 mg/l

The water treatment plant was cut into the system at 10:20 a.m., and was operated at one-third capacity. Activated carbon, Aqua Nuchar A, at the calculated rate of 60 mg/l was added using both the normal and auxiliary feeding facilities. The water was coagulated with alum and lime. Free residual chlorination was maintained at the water intake, but since free chlorine is effectively removed by the large dosages of carbon, additional chlorine was added at the clear well. Samples of finished water obtained at 11:00 and 11:50 a.m., showed that the raw water was being successfully treated with the predicted amounts of carbon. No fish toxicity could be found in either of these samples and the threshold odor number was 1.5 and < 1.0. Full operation of the water treatment plant was started at 4:00 p.m., and continued until 1:30 the next morning when the plant was shut down for the night. Water treatment was resumed at 8:15 a.m., on August 27.

Operation of the water plant unfortunately was not without mishap. A combination of two events conspired to make the first day less than completely successful. During the period 11:00 a.m., to 1:30 p.m., water entering the water plant was unusually heavily contaminated with the fish poison. Concentration of Pro-Noxfish rose sharply to greater than 6.4 mg/l and two samples showed threshold odor number of 90 and 74. At about the same time, unnoticed difficulty

* Trademark of West Virginia Pulp and Paper Company

with the auxiliary carbon feeder caused the carbon dosage to drop from 60 mg/l. to approximately 17 mg/l. These events allowed inadequately treated water to enter the distribution system. Finished water samples taken during the period 1:30 p.m., to 5:00 p.m., showed a rise in threshold odor number to a peak of 7.0 and a decline again to less than one when proper carbon treatment was resumed. During this period, two consumer complaints were received, the only ones during the entire operation.

SUMMARY OF RESULTS

Fish Toxicity

A summary of the laboratory data is presented in Figure 5. Except for the excessively high value of > 6.4 mg/l obtained in the early hours during poisoning of the reservoir, the concentration of Pro-Noxfish averaged 2.0 mg/l during the first day. Thereafter the concentration of Pro-Noxfish in the raw water decreased at a uniform rate until at the end of three days, less than 0.1 mg/l remained which was non-toxic to the test fish. A plot of percent Pro-Noxfish remaining versus elapsed time is linear on semi-logarithmic paper. From this curve the half-life of the rotenone compounds was shown to be less than one day, (0.75), under the conditions existing during the study. At no time during the entire study could any toxicity to

fish be detected in the treated water samples. A total of 12 samples were consistently non-toxic to the test fish during 24-hours of exposure.

Samples for determination of concentration of Pro-Noxfish were obtained from various areas and at various depths in the reservoir as shown in Figure 1. Unfortunately lack of time did not permit sampling during the first day. The data show, Table II, that by the second day excellent distribution of Pro-Noxfish had been achieved in the areas tested in the lake.

Odor-Raw Water

Uneven application of Pro-Noxfish near the raw water intake produced a slug of heavily contaminated water with threshold odor numbers ranging up to 90. If two high values are omitted, the average threshold odor number of the raw water the first day was 42. At the end of three days, odor had decreased to a threshold odor number of 5 although the odor typical of Pro-Noxfish was still discernible. The threshold odor number had decreased to 4 at the end of six days and no odor of solvent could be detected, but a marshy odor, characteristic of the raw water before fish poison had been added, was observed.

TABLE II

DISTRIBUTION OF PRO-NOXFISH IN
DICKINSON RESERVOIR

DATE	AREA	DEPTH-FT.	TEMP.°C	PRO-NOXFISH CONC.mg/l
8-27-58	2	Surface	19.9	0.82
"	2	12	19.8	0.90
"	2	25	19.7	0.94
"	4	Surface	19.8	0.86
"	4	5	20.0	0.84
"	4	10	20.4	0.84
8-28-58	2	Surface	19.8	0.65
"	2	12	20.0	0.70
"	2	24	20.1	0.78
"	4	Surface	20.0	0.53
"	4	5	20.1	0.43
"	4	10	20.0	0.57
"	7	Surface	20.0	0.65
"	8	Surface	20.0	0.57

Activated Carbon Dosages

Determination of Pro-Noxfish content of the raw water by fish bioassay and by threshold odor number provided the means to predict the amount of carbon required by reference to the carbon dosage chart shown in Figure 4. These data are shown in Table III. Good control of the applied carbon dosages compared to predicted was maintained during the first three days. Excessive amounts of carbon were applied on the following days because of a combination of events. During this period, threshold odor number was dropping very rapidly and water usage was being curtailed because of the onset of cooler weather. The lag in time introduced by the collection and analysis of the samples and the fact that the improvised activated carbon feeder could not be accurately controlled also account for the high carbon dosages. At the end of seven days it was possible to reduce the carbon dosages to the normal amounts of 3-4 mg/l used before the fish killing operation.

Odor-Finished Water

When sufficient activated carbon, as predicted from raw water analyses, was actually applied, water with a threshold odor number of one or less was invariably produced. On two occasions, inadequate carbon treatment immediately resulted in finished water with threshold odor numbers greater than one.

TABLE III
PREDICTED AND APPLIED ACTIVATED
CARBON DOSAGES

DATE	8-26	8-27	8-28	8-29	8-30	8-31	9-1
	Mg/l Activated Carbon						
Average T. O. Number	42	35	35	5	3	4	4
Carbon Required mg/l	61	52	52	10	8	9	9
Average Pro-Noxfish mg/l	2.0	1.5	0.7	0.18	<0.1	-	-
Average Carbon Applied mg/l	61	53	48	36	23	18	12

The causes of the high threshold odor values during the first day have been discussed above. On August 28th, two days after the application of the fish poison, a rise in threshold odor number of the finished water to a maximum of 3.5 was observed. This lapse in adequate treatment occurred because a constant amount of carbon was being added during a period when water pumpage was at its maximum during the time of the study. An average of 48 mg/l of carbon was applied when the predicted requirement was 52 mg/l as shown in Table III. No consumer complaints occurred during this period since dilution in the distribution system served to reduce the threshold odor number at the household water tap. A limited number of samples were obtained from various points in the distribution system and are shown in Table IV.

TABLE IV
THRESHOLD ODOR NUMBERS OF SAMPLES
FROM DISTRIBUTION SYSTEM

DATE	DISTANCE FROM WATER TREATMENT PLANT- FEET	AVG. THRESHOLD ODOR NO.
8-28	3500	2
"	3800	2
"	7400	2
"	8100	< 1
8-29	3500	< 1
"	3800	< 1
"	7400	< 1
"	8100	< 1

Water Plant Data

Data shown in Table V summarize the chemical characteristics of raw and tap water both before and during the fish killing operation. The listed chemical and physical qualities of the water were not affected with the exception of raw water turbidity which showed a steady decrease to a minimum of 1 on September 23 (not shown in Table). Eradication of the fish which stir the bottom mud probably accounts for the clarification of the lake.

TABLE V
SUMMARY OF PLANT DATA

DATE		BEFORE		AFTER ADDITION OF FISH POISON						
		8-24	8-25	8-26	8-27	8-28	8-29	8-30	8-31	9-1
		WATER ANALYSES mg/l								
T. Hardness ⁽¹⁾	Raw	98	98	98	99	99	99	98	98	97
	Tap	83	100	122	103	96	103	92	118	104
Alkalinity ⁽¹⁾	Raw	158	156	168	157	157	157	170	180	168
	Tap	134	156	156	157	138	154	140	158	155
pH ⁽²⁾	Raw	8.1	8.1	8.1	8.1	8.1	8.1	8.5	8.3	8.1
	Tap	8.9	8.9	8.9	8.9	8.9	8.9	8.9	8.9	8.9
Turbidity ⁽²⁾	Raw	25	25	80	30	25	25	22	10	12
	Tap	0	0	0	0	0	0	0	0	0
Free Chlorine	Tap	0.5	0.5	1.0	0.75	0.75	0.5	1.0	1.0	0.9
Fluoride	Tap	1.2	1.2	-	1.2	1.2	1.2	1.2	1.2	1.2
Temp. °F	Raw	72	72	71	72	72	72	65	70	69
		CHEMICALS ADDED mg/l								
Alum		69	60	68	73	73	60	45	71	65
Lime		88	80	81	73	80	77	76	71	52
Hydrofluorosilicic Acid		1.1	1.4	0.85	0.88	1.1	1.0	0.95	1.2	1.1
Polyphosphate		2.0	2.0	2.2	2.2	1.5	1.9	2.1	2.1	12
Activated Carbon		3.4	7.0	61	53	48	36	23	18	12
Chlorine		7.3	8.9	10	7.8	9.5	8.0	9.1	7.1	8.3

(a) (1) Expressed as calcium carbonate

(2) Expressed as units

Considerable amounts of carbon were carried over from the flocculator on to the sand filters, but without any detriment to the filter runs. Before addition of fish toxicant, filter runs averaged about 42-hours while runs during the project ranged from 27 to 66 hours with an average of 46 hours.

During the period August 26 to September 1 when activated carbon dosages greater than normal were required a total of 2,400 pounds was added. At 16 cents per pound, the cost of activated carbon for removal of toxicity and odor of 2.0 mg/l of Pro-Noxfish amounted to \$384.00. Since at this time of the year the normal use of carbon averaged about 3 mg/l, the net cost of chemicals to the water treatment plant attributable to the fish killing operation becomes \$354.00.

CARBON FILTERS

(3)

Carbon filters, installed on the raw water line at the dam site just prior to the point of chlorination and on the finished water line at the water treatment plant, were operated before, during and after the fish killing operation. The concentration of chloroform extractable organic material from these filters is shown in Table VI.

TABLE VI

CONCENTRATION OF CHLOROFORM EXTRACTABLE
ORGANIC CHEMICALS IN RAW AND FINISHED WATERS

DATES OF FILTER OPERATION	CHLOROFORM EXTRACTABLES - MICROGRAMS PER LITER	
	RAW	FINISHED
Aug. 13-Aug. 23	46	75
Aug. 26-Sep. 26	435	38
Oct. 1-Nov. 5	151	75

Concentrations of chloroform extractable organic material in both the raw and finished waters of the first pair of samples are what might be expected from an unpolluted surface water where materials of natural origin are invariably present. A quantity of light oily material suggestive of lubricating oil produced the apparent anomaly of more organic material in the finished water than in the raw water sample. The almost tenfold increase of organics in the raw water obtained during and for some time after the fish kill operation confirms the application of the fish poison. More revealing, however, is the low value for the finished water during this period, ample evidence of the effectiveness with which the water plant removed the contaminating fish poison. Increased organic content of the raw water obtained a month following the fish kill operation probably reflects

decomposition of poisoned fish which had not been harvested.

Finished water quality, as reflected by its organic content, remained unchanged from the period prior to the fish kill.

Further evidence of the efficiency of the water plant in removing the fish poison is provided by infrared spectrograms which were obtained on all of the raw and finished water chloroform extracts, and on the fish poison itself. Selected spectrograms are shown in Figure 6. Spectrogram Number 1 prepared from the chloroform extract of the raw water prior to the fish poison application shows no fine structure and is typical of the kind of spectrogram obtained from a complex mixture of organic material normally present in an unpolluted surface water. Spectrogram Number 2 from the raw water during the fish kill operation, however, exhibits many well defined peaks. Indeed, the striking similarity of this spectrogram with that obtained on Pro-Noxfish, Spectrogram Number 3, is convincing evidence of the presence of this fish poison in the raw water extract. Spectrogram Number 4 of the extract from finished water obtained during the fish kill operation shows no evidences of the presence of fish poison. Efficient removal at the water plant had reduced the residues to undetectable amounts. Spectrogram Number 5 obtained on the extract of raw water more than a month following the fish kill operation shows no detectable change from Spectrogram Number 1.

SUMMARY AND CONCLUSION

During the period August 26 to September 1, 1958, the water treatment plant in Dickinson, N. D., successfully treated water which had been contaminated with an average of 2.0 mg/l of a fish poison.

Fifty-five hundred gallons of Pro-Noxfish, a commercial fish poison formulation, were added to Dickinson Reservoir, volume approximately 5,800 acre feet, as the first step in fish management program. Treatment at the water plant consisted of adding 61 mg/l of activated carbon which effectively reduced the toxic and odorous components to safe and palatable levels. This dosage was predicted as adequate by laboratory study. The components toxic to fish decomposed at a rapid and uniform rate and could not be detected in the raw water at the end of three days. The odor component of Pro-Noxfish dissipated more slowly, but it also could not be detected at the end of six days. During this time, decreasing dosages of carbon were required for proper treatment of the water. Except for two instances when raw water was known to be treated with inadequate amounts of carbon, finished water had a threshold odor number of less than one, and was uniformly non-toxic to fish. No operational difficulties were encountered in the water treatment plant and operation of the plant was back to normal within eight days. The cost of activated carbon required during this period in excess of that normally used was \$354.

A carbon filter study of the entire operation showed that the water plant had effectively removed the components of the fish poison from the raw water. Corroborative evidence was obtained by infrared confirmation both of the presence of the fish poison in the raw water and its absence in the finished water. No change could be detected in the quality of the raw water, a month after the fish killing operation.

Consumer acceptance of the water was good. Except for two complaints received during the first day following an operational failure, no other objections were received at the plant. Public acceptance was facilitated by news coverage by the local newspaper which had prepared the public for a possible slight taste in the water. Random questioning of townspeople revealed that while most consumers detected no odors in the water a few individuals were aware of the "kerosene-like" flavor, which was not unexpected since a residual threshold odor number of one presumes that some odor is detectable.

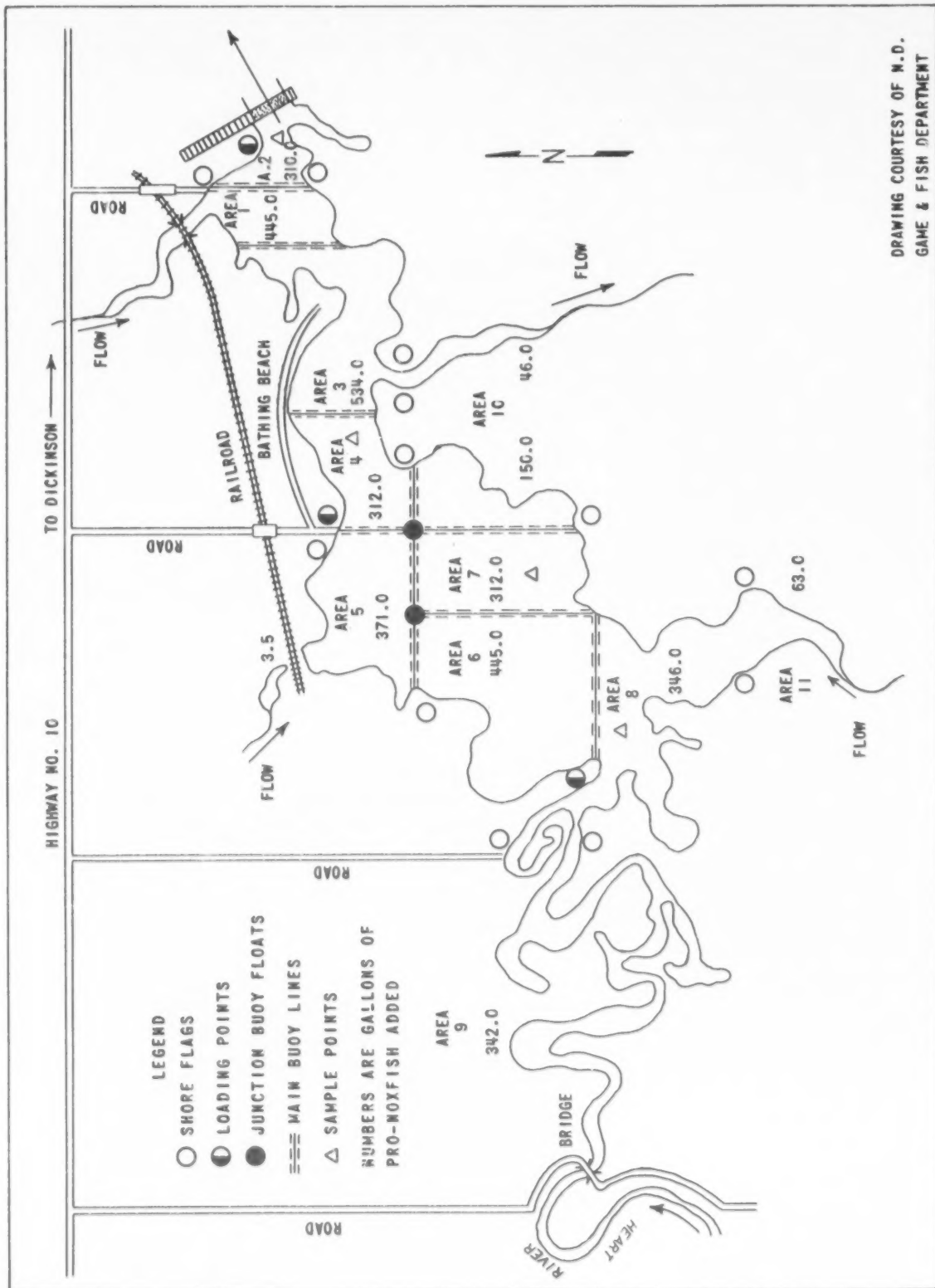
This study substantially confirmed the predictions of laboratory studies that with adequate activated carbon treatment a water treatment plant is fully capable of producing safe and palatable water from a supply which has been contaminated with a fish poison formulation.

ACKNOWLEDGMENT

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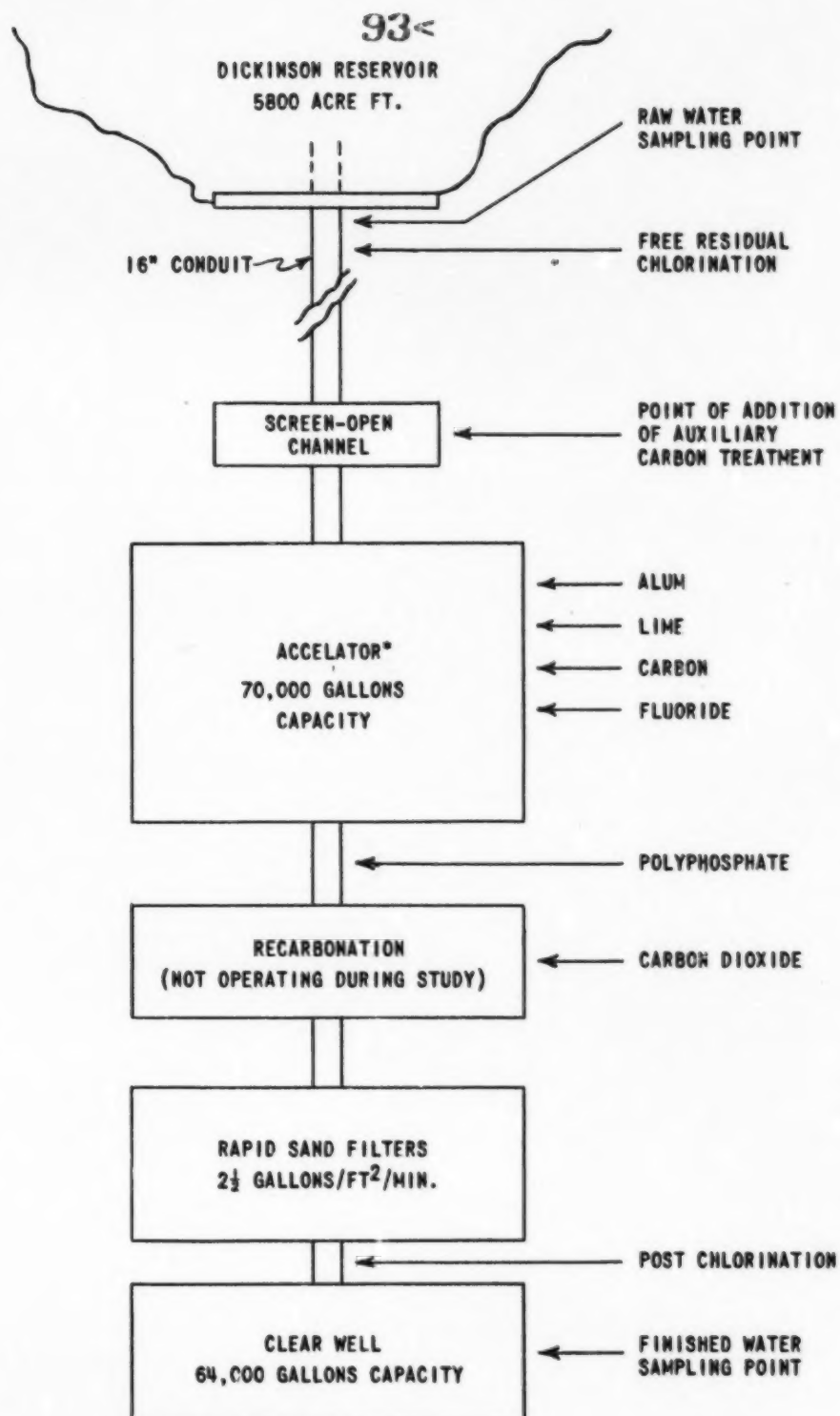
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GAME & FISH DEPARTMENT

DICKINSON RESERVOIR
ERADICATION PROJECT

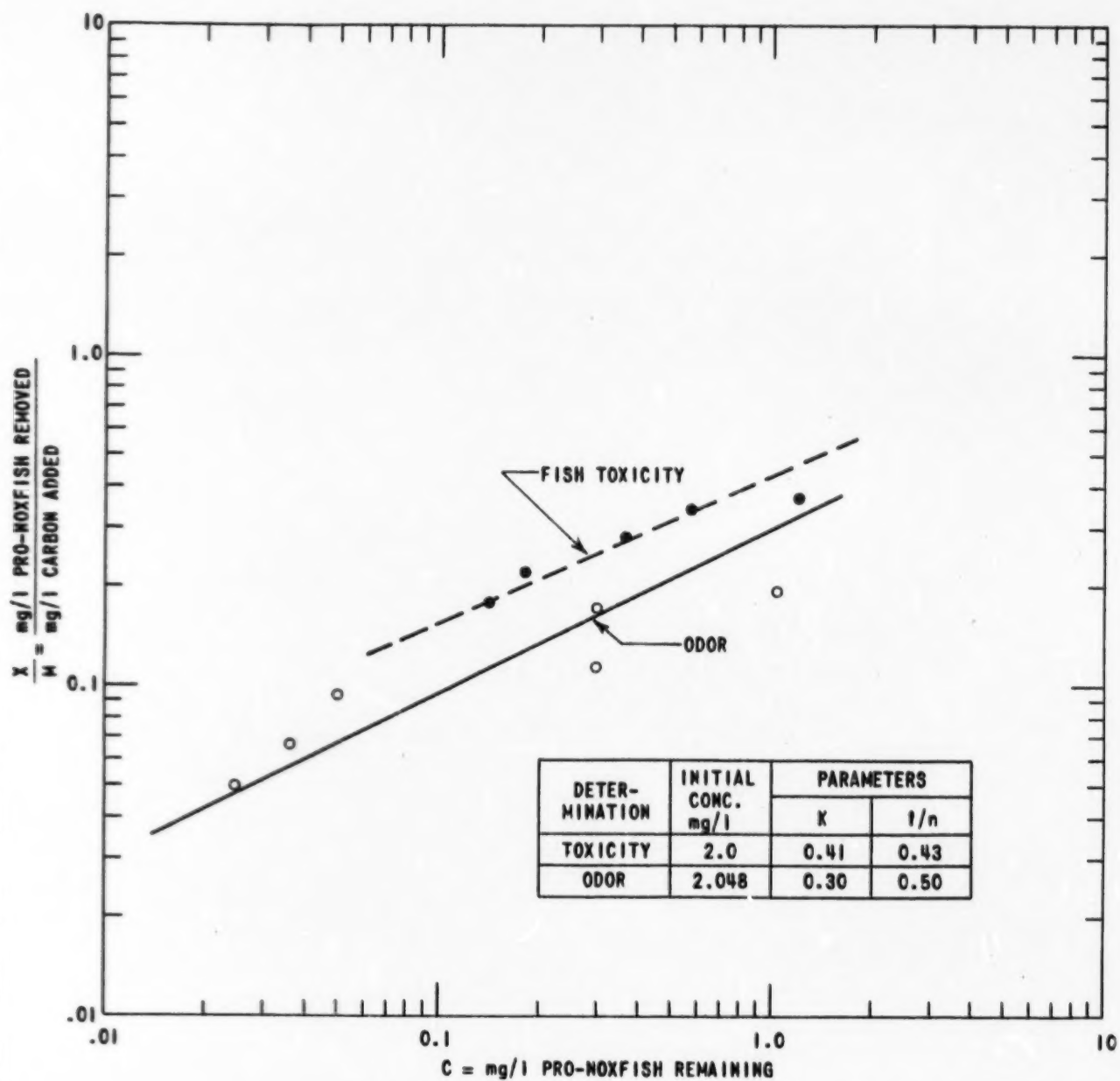
FIGURE 1



*TRADEMARK OF INFILCO, INC.

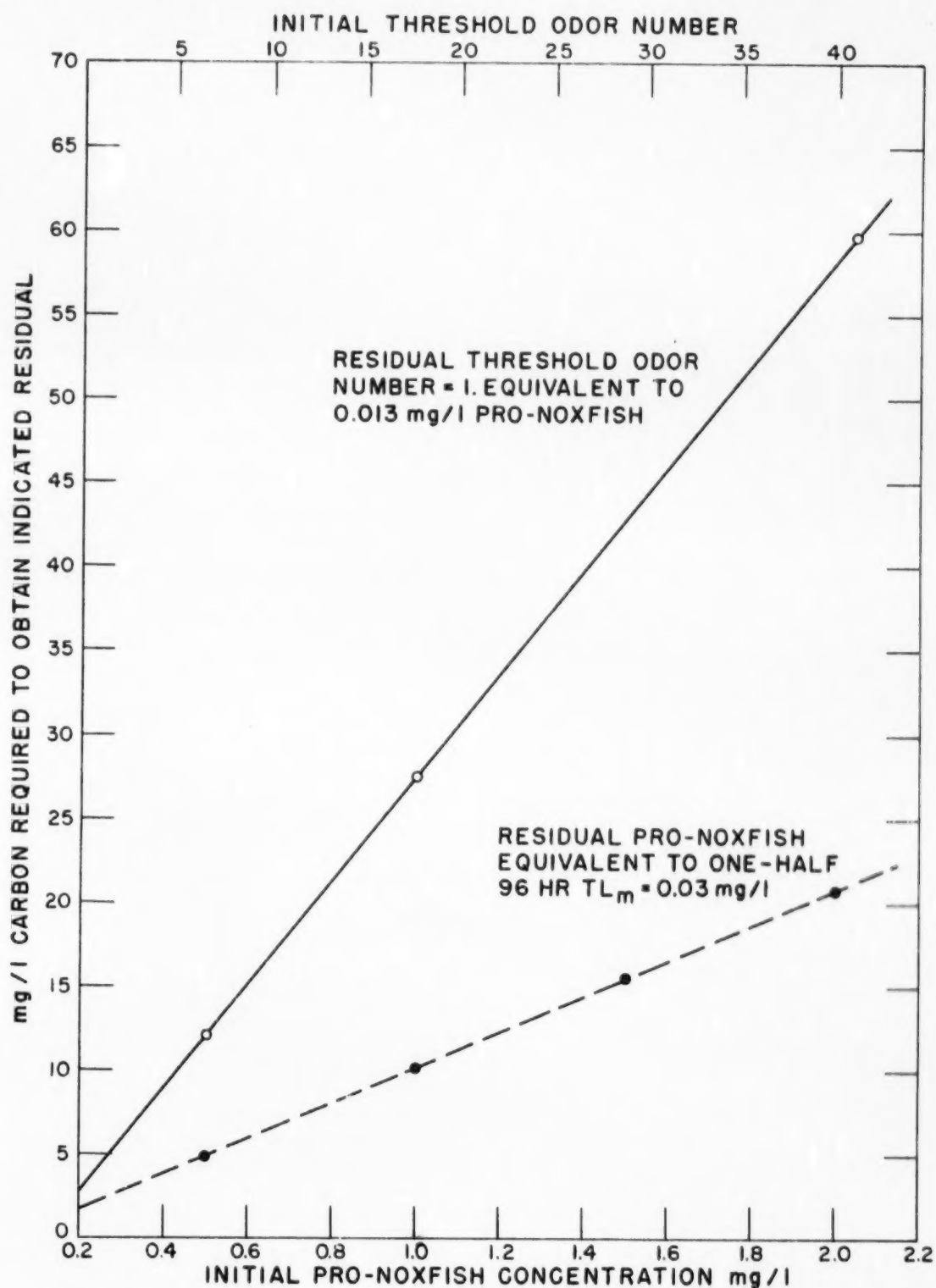
SCHEMATIC DRAWING OF DICKINSON, N.D. WATER TREATMENT PLANT

Figure 2



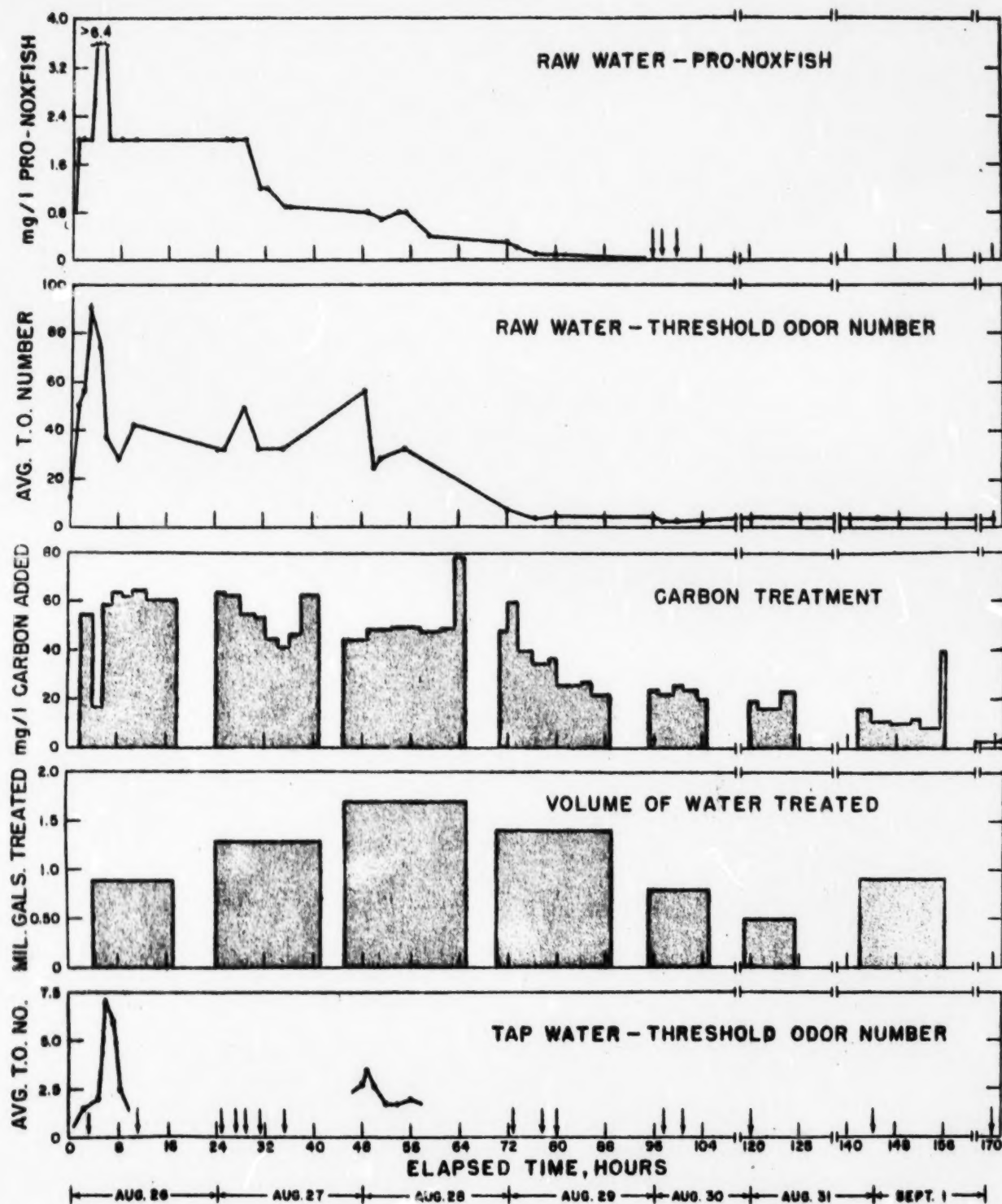
CARBON ADSORPTION ISOTHERMS FOR PRO-NOXFISH

Figure 3



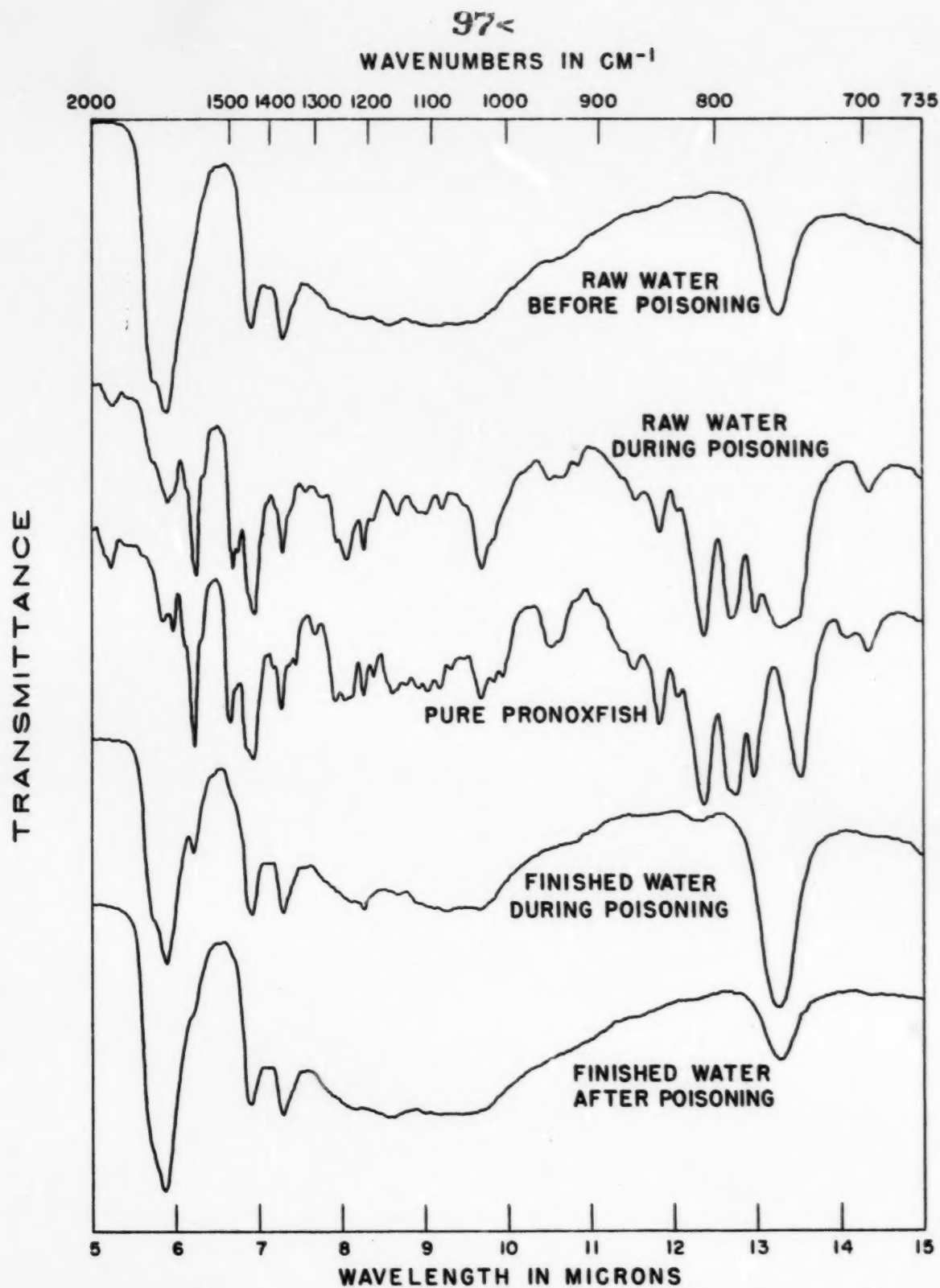
CARBON DOSAGE CHART FOR REMOVAL OF PRO-NOXFISH

FIGURE 4



LABORATORY DATA AT DICKINSON WATER TREATMENT PLANT

FIGURE 5



INFRARED SPECTRA OF CARBON FILTER EXTRACTS
FIGURE 6